THE MANUFACTURE OF CHEMICAL MANURES

BY

J. FRITSCH

TRANSLATED FROM THE FRENCH

SECOND ENGLISH EDITION, REVISED AND ENLARGED

BY

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PREFACE.

THE manufacture of chemical manures has now become a most important industry in several countries, but notwithstanding the magnitude of this industry, up to the issue of the first edition of this book, very little had been written on the subject in France, and no author in that country had attempted to make it the matter of a special treatise. By the issue of this book the author endeavoured to fill what must have been a long-felt want.

From a technical point of view French literature supplies but little material for such purpose. French managers and chemists rarely publish their knowledge (but this applies also more or less to other countries), either they have not the time or they are bound down by the conditions of their employment not to disclose matters which are regarded as secrets that may be useful to competitors. This is in many cases a grave mistake since those adopting this plan work in a little groove which becomes deeper and deeper; as against this idea it is evident, however closely that it may be kept, knowledge eventually becomes universal.

Other countries, especially Germany, are better off in this respect, since foreign publications are to be obtained, including several special treatises, annual reports on the progress of different industries, edited in most cases by retired works managers or other practical men, etc., in which the different processes are described and discussed in all their bearings, due note being taken of new processes or discoveries.

From such material, together with personal experience, and also with the help of knowledge imparted by eminent specialists and scientists who have given every aid and encouragement, the author has prepared the present book, which, although it lays no claim to be a perfect and complete compendium of the whole subject, is nevertheless, a true and

we hope readable account of this most important industry, which should be useful not only to manure manufacturers, but also to farmers, agricultural chemists and others interested in agricultural matters.

The first edition of this book was published in France in 1909, and an authorized translation, prepared by Donald Grant, was issued by the present publishers in 1911. In that edition many practical notes were added by the translator, from a store gathered in a long career as chemist and works manager in chemical manure and sulphuric acid works. These notes have been retained for the most part in the present edition but have been, except in a few cases, incorporated with the text. In addition the matter has been closely revised, and much new material has been added, in order to bring it thoroughly up to date. Two other books by the publishers also dealing with the subject may be referred to, these are "Bone Products and Manures," by Thomas Lambert; and "Utilization of Waste Products," by Theodor Köller.

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CHAPTER I.

PHOSPHORIC ACID.

History.—The discovery of phosphorus is due to the alchemists. In 1669, Brand, a Hamburg merchant, searching for the philosopher's stone in human urine, discovered an interesting substance which he called *phosphorus*, i.e. a light bearing substance, luminous in the dark. All the phosphori known up to that time—and there was quite a series of them—to become luminous needed previous exposure to sunlight, and yet their luminosity soon vanished, whilst the new substance emitted light spontaneously, and preserved that property permanently. It was, therefore, termed *phosphorus*. Brand kept his process secret at least for a time, but it is stated that he sold the secret to Krafft, who imparted it to Kunkel, a Berlin chemist, who described the method of preparation. In 1688, Albinus extracted phosphorus from mustard seed and cress seed. Thus within a few years phosphorus was found in both the animal and vegetable kingdoms without, however, anyone dreaming of its connexion with inorganic nature. According to the cosmic theories of the times this substance was held to be the product of other substances, or even the result of spontaneous generation under the influence of ill-defined vital forces. The scientists of the time had not yet distinguished the chemical elements, the very simple theory of which was destined in the future to furnish the very basis of the science of these products.

It is interesting, however, to observe that free phosphorus was prepared and examined during seventy years without its compound with oxygen, phosphoric acid, from which it had been isolated and to which it so easily reverts, being known. Phosphoric acid was not discovered till 1743, by Margraff, who ascertained its exact nature and succeeded in re-converting it into phosphorus by calcining it with charcoal. In 1769, Gahn, a Swedish chemist, found this acid in bones, and a few years later Scheele, his countryman, published a process by which phosphorus could be extracted from bones, which is still used in its main features.[1] Ten years after the

[1] Scheele was by birth a Prussian. See Scheele's "Chemical Essays," Scott, Greenwood & Son.

discovery of phosphoric acid in bones, and more than 100 years after the first preparation of phosphorus, Gahn found this substance in the mineral kingdom also, viz. in lead phosphate (pyromorphite); Vauquelin and Klaproth soon afterwards found phosphoric acid in apatite, that beautiful mineral, met with in large masses, the composition of which is analogous to the mineral constituent of bone. Such briefly summarized are the chief historical facts regarding the discovery of phosphorus and phosphoric acid in the three kingdoms of nature. Since those times chemists have continued their investigations; they have searched for this substance everywhere, and have found it more widely distributed as analytical methods have been improved. Its presence in urine and in bones led to the assumption that it might be present in all the fluids and organs of man and animals, and very soon this was found to be the case. It was found in all plants and in all their organs. It was thenceforth recognized that the phosphorus contained in the body of animals was of vegetable origin. But from whence do plants derive this substance? The answer to this question was sought for a long time. Even up to the middle of the eighteenth century, when scientists like Saussure (1740-1799) and others were led by simple logic to search for phosphoric acid in the soil, agronomists persisted in regarding it as derived from other substances, since very little of it was found in the soil, and this little might very well be brought on to the land by farmyard dung. However, improved analytical methods gradually elicited the truth.

Origin and Distribution of Phosphoric Acid in Nature.—If it be interesting for the farmer and the chemist to follow the migrations of one constituent of the air, and the curious phenomena under the influence of which the molecule of nitrogen becomes successively ammonia or nitric acid, then vegetable organism, then finally muscular fibre, it is none the less instructive to follow the migrations of the molecule of phosphorus. Let us endeavour to grasp these migrations, and to trace them, starting from the point of origin of phosphoric acid, i.e. the presence of this substance in the primitive and crystalline rocks. The analysis of the primitive rocks, and of the metalliferous veins, which they contain, proves that phosphoric acid is almost always one of their constituent elements.[1] Associated with lime, the oxides of iron, manganese, lead

[1] The two men of science who studied the question most profoundly were Forchammer of Copenhagen and Stockhardt of Germany. The latter found phosphoric acid in several rocks in which it was believed to be absent. The percentages of phosphoric found in different rocks are given in Table I. opposite.

and copper, this substance constantly reveals its presence to the expert chemist who makes a special search for it. The proportions present are most often very minute, but that is a matter of little importance since plants have a marvellous faculty of freeing from the soil the principles necessary to their development. And let us remark with Bobierre, "how everything hangs on a chain to explain to us the distribution of phosphoric acid in our crops. Let us go back, in imagination, to the origin of things, to those great natural phenomena, all the traditions in regard to which are in accordance with what geology reveals to us of these gigantic phases. The igneous rocks contain phosphoric acid. The disintegration of these rocks under the combined influence of water, air, heat, and carbonic acid, soon favours the physical division of the rock masses. Vegetation develops, vivacious, luxuriant, immense, accumulating at the same time both carbon from the atmosphere—which it is to return as coal to far-off generations—and phosphates which its organs, immersed in a virgin soil, assimilate to abandon later in a fine state of division on the surface of the soil. And as an energetic, active, incessant medium of this providential distribution, the animal world supervened with its powerful capacity of condensation of principles, rich in phosphorus and in nitrogen. Thus it is that vegetation supplies phosphates in a readily assimilable form for the alimentary needs of new individuals. The molecule of phosphoric acid is no longer the inert crystalline portion of the igneous rock, it is no longer the mineral framework of the plant, it is the osseous substance of the animal, it is both its skeleton and its flesh, its nervous fibre, and its entire being. Our ideas of the organism and of phosphorus are inseparable the one from the other."

The beds of the different geological formations all contain fossils, more or less rich in phosphoric acid. The Cambrian yields *Lingulides* and *Discenides*, forerunners of the *Brachiopods*, whose calcareous shells were comparatively rich in phosphoric acid. At

TABLE I.—PERCENTAGE OF PHOSPHORIC ACID IN VARIOUS ROCKS.

Rock.	Per cent.	Rock.	Per cent.
Felspar (Rochsbourg) .	1·70	Melaphyre (Plauen)	0·38
Gneiss (Gerlusdorf) .	0·78	Syenite (Plauen) .	0·18
Granulet (Penig) . .	0·62	Gneiss (Tharandt)	0·25
Granite (Hellsdorf) .	0·58	Felsite (Tharandt) . .	0·21
,, (Burgstaldt) .	0·68	Limestone (Schweindorf) .	0·51
Basalt (Tharandt) . .	1·10		

a later period vertebrata appear; first, the Silurian fish, then the saurians of the Carboniferous and Permian, and finally, the birds (Jurassic) and mammals (Trias), the skeletons of which form the principal elements of the accumulation of phosphoric acid. Thus the soil of all periods may contain phosphates, but they are not found in large quantity except in certain formations and under peculiarly favourable circumstances, which we vaguely perceive, but of which it is impossible to give a really satisfactory explanation. The solution of phosphate of lime acid by rain water, charged with carbonic acid, traversing the superficial layer of soil covered with vegetation and thus rich in humus, its entrainment into the subsoil, and its accumulation in the subjacent rock, by loss of carbonic acid —such seems to be the genesis of phosphate deposits. On the phosphate beds so formed new layers of phosphates were deposited as soon as the carbonic acid acting as the solvent had set free sedimentary phosphates. When the solution percolated into hollows it formed pockets. The carbonated water could even convert already formed phosphate into a special form, for example that of vitreous staffelite. Nodules were formed when the rock to which the phosphoric acid was combined was deficient in consistency, or had become porous, for example owing to the upheaval of the deposit, the different portions of which were washed and removed by water, thus rounding the fragments. Nodules may again be formed by the fixation of phosphate of lime round a nucleus, for example around grains of sand swimming in the solution on the impulse of a crystal growing in an appropriate solution, or organisms or even bells of gas rising in the solution drawing to it particles of the same nature as itself. Finally, another hypothesis of the formation of nodules is that precipitated phosphate of lime had been gradually reunited into compact nuclei by water through the intervention of pebbles of silica. Apatite was the first phosphate formed by the crystallization of the incandescent rocky magma. Its crystalline form is hexagonal. As it cooled slowly, the mass of liquid apatite formed crystals of different sizes, varying from capillary needles, scarcely visible, up to 12 in. in length. Their interior always assumes a lamellar structure. Apatite is found massive, with this crystalline structure, or even compact and massive when it is embedded in basalts. But compact massive apatite is practically indistinctly crystalline apatite. Pseudo-apatite is disintegrated apatite. All these forms of phosphate, from the crystalline form to the amorphous, from isolated nodules to rock phosphate, are derived from an identical origin. Summing up, phosphorus existed in the beginning of things in the primitive rocks. It has become more easily assimilable in virtue of its distribution in sedimentary and transported soils; vegetables have absorbed it, then they have given it up to the animals, which have condensed

and accumulated it in numerous points of the globe. Let us note, with Buckland, how astonishing it is that the human race should, for so many centuries, have remained ignorant of the fact that a considerable portion of the surface of the globe was formed by the debris of the animals which inhabited the ancient seas. There exists, according to the same author, vast plains and enormous mountains, which are merely, so to speak, the charnel houses of preceding generations, in which the petrified debris of extinct animals and vegetables are piled up to form marvellous monuments. These monuments attest the work of life and death during incalculable periods. Cuvier, appreciating these curious natural phenomena, declared that the sight of such a spectacle as that of the debris of life forming almost the whole of the soil on which we tread appeared so terrible that it was difficult for him to concentrate his imagination on the causes which have produced such great effects. These effects, so terrifying to the genius of Cuvier, are really only the result of one and the same cause—an efficient cause, which is confirmed under the most diverse conditions, and in all latitudes, with a wonderful unity of design. Only the Sovereign Master of Life and Death could accomplish such wonders.

Let us now try to find the amount of phosphoric acid in different media—phosphoric acid in the soil, in plants and animals. About the time when British agronomists[1] were exploring the deposits of phosphate of lime of Estramadura, it was discovered, in Surrey, that the use of ground bones, and other substances rich in phosphoric acid, produced no beneficial result when applied to soils, fertile enough in themselves, the subsoil of which belonged to certain deposits of the lower and upper Greensand. This led to the supposition that phosphate of lime, which is one of the fertilizing constituents of ground bones, is naturally present in these soils in sufficient proportion. Mr. J. C. Nesbit, an expert chemist, immediately collected the soils and rocks of these districts so as to ascertain the cause of their fertility. Amongst others, he received from Farnham samples of a fertile marl, situated on the property of Mr. J. M. Paine. A rapid examination showed the presence, in this marl, of an unusual amount of phosphoric acid, and in November, 1847, he informed Mr. Paine of this discovery.[2] From this marl

[1] This very evidently refers to Dr. Daubeny, who inspected and reported on these deposits (Estramadura) in 1843. His report is printed in the "Journal of the Royal Agricultural Society of England," Vol. V, Part II.—Tr.

[2] But Mr. Paine himself, in conjunction with Professor Way, the chemist of the Royal Agricultural Society of England, in 1848 published the results of their combined elaborate researches on the phosphoric strata of the chalk formation in a paper in the "Journal of the Royal Agricultural Society of England," Vol. IX, Part I, pp. 56-84. The reader is referred to this memoir; suffice it to mention here that the marl contains nodules much richer in phosphate of lime than the marl in which they are disseminated.—Tr.

28 per cent of phosphoric acid, corresponding to 60·67 of phosphate of lime, was extracted. The general mass of the marl contained 2 to 3 per cent of phosphoric acid, equal to 4·33 to 6·5 per cent of phosphate. It will be seen that in presence of such a proportion of phosphoric acid the application of phosphatic manures was quite superfluous. In the *Tchermo Sem*, so fertile in Russia, where from time immemorial the highest yields of wheat have been obtained without any manure, 0·6 per cent of phosphoric acid is present, whilst mediocre soils only contain 0·1 ; fertile soils, 0·2 to 0·5 ; very fertile soils, 0·8 and upwards. Regarded by themselves these figures appear very small, but applied to a given surface, they are considerable. A hectare of arable land, say 2·5 acres, with a depth of 0·2 metre, say 10 in., weighs 5000 tons, say 2000 tons per acre, and if such soil contains 0·6 per cent of phosphoric acid that equals 30 tons of that acid per hectare or 12 tons per acre. The diffusion of phosphoric acid in arable land responds, moreover, to a providential law, that element being as indispensable to plant life as to animal life. In the absence of phosphoric acid, none of our cultivated plants can pass through all the phases of vegetation ; the seed may germinate, produce leaves, stem, branches, but these organs remain attenuated, lingering, till the plant dies prematurely without bearing flowers or fruit. Corenwinder made researches to trace the phosphorus in plants. Analyses of roots, stem, and fruit proved that phosphorus exists in nascent organs where it contributes to organization. It diminishes proportionally in the root; thus the root of beet-root does not contain phosphorus after the maturity of the seed. It is to be found principally in the seed. Corenwinder found that in the pollen of flowers there is a considerable amount of organic phosphorus recovered as phosphoric acid in the ash of these minute cellules. In this respect pollen is analogous to the seminal fluid. Saussure and, later, Garreau, Professor of Botany at Lille, pointed out that the leaves of a tree yield, on burning, ashes richer in phosphorus than at any other epoch of vegetation. If now we gradually ascend to the examination of animals, we find that their bones, their muscles, their nervous and cerebral substance, the fluids of their tissues, blood, milk, urine, seminal fluid, contain always and everywhere phosphorus in some form or other. Intimately associated with organic substances, phosphorus abounds in the cerebral mass and the nervous system. One may almost say that it is organized. Combined with oxygen and lime it forms one of the important elements of the skeleton. Dissolved by the animal fluids, it is unceasingly carried from one point to the other of the individual, and if its total amount remains fixed, for a given animal, its molecules nevertheless displaced by solvent or vital actions is excreted, then replaced by new molecules absorbed by the digestive system. To remove phosphoric acid and

lime from the diet and try to nourish an animal on purely nitrogenous substances would lead very quickly to a termination of its life. The animal in this respect behaves like the plant (Bobierre). Thousands of analyses made in recent years by Thezard show that, amongst invalids, the elimination of phosphoric acid through the urine follows a progress parallel to that of the disease. The further the latter progresses the more does the phosphate content of the urine increase; in these conditions when the loss resulting from the elimination cannot be repaired by a diet appropriate to the needs of the individual, the human organism perishes with astonishing rapidity, this has led to phosphoric acid being regarded as the vital element *par excellence*. According to Elie de Beaumont, a human skeleton weighs, on an average, 4·6 kg., say 10 lb., and assuming that human bones contain 53·04 per cent of phosphate of lime, a skeleton ought to contain 2·44 kg., say $5\frac{1}{4}$ lb. But a human body weighs, on an average, 75 kg., say 165 lb.; deducting the weight of the skeleton there remains 70 kg., say 154 lb. of soft parts, which on incineration yield, like ox-beef, 1·5 per cent of ash entirely composed of phosphate of soda, potash or lime, and alkaline chlorides. The amount of phosphoric acid which they contain may be taken as equal to an amount of phosphate of lime equal to 80 per cent of the weight of the ash, or to 1·5 per cent of the weight of the soft parts multiplied by 0·8, say 840 grm. These 840 grm. added to the 2·440 kg. contained in bones, give a total of 3·28 kg. of phosphate of lime, say 1·439 kg. of phosphoric acid or 639 grm. of pure phosphorus. These figures show the importance of the rôle which phosphoric acid plays in the support of life on the globe. They ought to teach us also, to use, with wise foresight, the stores of phosphoric acid with which bygone ages have endowed us, since, no matter what may be the importance of the deposits now known and exploited, and even of those which may be discovered in the future, they are far from being inexhaustible; besides there is the danger of dispersion of phosphoric acid by default of restitution to the soil, which is more threatening for a future less distant than that of the dispersion of nitrogen and potash.

Properties of Phosphorus.—(1) *Physical Properties.*—Phosphorus obtained by Scheele's method, i.e. by the distillation of phosphate of lime and charcoal, is a cream coloured translucent body. It is found in commerce mainly in the form of sticks. At the ordinary temperature it is soft like wax, brittle in the cold. It has the odour of garlic. Its density varies between 1·82 and 1·84. It is insoluble in water and in alcohol, very soluble in essential oils, ether, benzol, carbon disulphide, sulphur chloride, and phosphorus chloride.[1]

[1] The solution of phosphorus in carbon disulphide was used by the Irish Fenians to burn the farms of their countrymen who were refractory to the Land League. This solution evaporates spontaneously and leaves phosphorus in a

Phosphorus melts at a temperature of 44·2° C., forming a colourless, oily liquid; if melted phosphorus be rapidly cooled it is converted into a black mass with a metallic appearance; if, on the contrary, the molten mass be still further heated—up to a temperature of 250°-260° C.—out of contact with air it is converted into a red modification which, at 280° C., reverts to the ordinary form. Phosphorus is highly poisonous. The absorption of a few centigrammes suffices to produce the death of a man by the excitation of the nervous centres which it produces. The antidote to phosphorus poisoning is spirits of turpentine. The vapours of phosphorus frequently respired induce necrosis of the bones, chiefly those of the face. The ordinary phosphorus industry and the manufacture of matches are amongst the most unhealthy of unsanitary trades. *Chemical Properties.*—(2) Ordinary phosphorus oxidizes slowly in the air, this oxidation being accompanied by a phosphorescent glow, from which phosphorus takes its name. In the open air, even cutting it with a knife will inflame it, owing to the generation of heat by the friction; that is why it should be cut under water. Chemically combined oxygen exercises on phosphorus the same oxidizing action as free oxygen. Water, which is a very stable compound of oxygen and hydrogen, is destroyed, though slowly, by this substance with formation of phosphoric acid and phosphoretted hydrogen. The transformation is more rapid when the water is rendered alkaline by caustic potash, soda, or lime. Nitric acid oxidizes phosphorus very energetically, converting it mostly into phosphoric acid. Owing to its great affinity for oxygen, phosphorus is never found in nature in the free state, it is always met with as phosphoric acid combined with bases.

Oxygenated Compounds of Phosphorus.—Phosphorus forms with oxygen and hydrogen the following anhydrides and acids:—

	Anhydrides.	Acids.
Hypophosphorus acid		H_3PO_2
Phosphorus acid	P_2O_3	H_3PO_3
Phosphoric acid	P_2O_5	H_3PO_4

There are three phosphoric acids known, viz.:—

Metaphosphoric acid $H_2OP_2O_5 = HPO_3$
Pyrophosphoric acid $2H_2OP_2O_5 = H_4P_2O_7$
Orthophosphoric acid $3H_2OP_2O_5 = H_3PO_4$

state of extremely fine division. The phosphorus then inflames spontaneously. If wooden objects be coated with a solution of Fenian fire nothing can prevent a conflagration. The solution of phosphorus in carbon disulphide, mixed with sulphur chloride, can be preserved well in close vessels but inflames with violence if a few drops of ammonia are allowed to fall thereon. This is the Lorraine fire of Nickles of 1869. Care must be taken to work in the open air on small quantities and to pour the ammonia by aid of a long tube. The new Lorraine fire of P. Guyot, 1871, is a solution of phosphorus in carbon disulphide to which sulphur bromide has been added. It inflames in 1 or 2 minutes after ammonia has been added.

Hypophosphorous acid is monobasic, that is to say, only one of its atoms of hydrogen can be replaced by a metallic atom. Phosphorous acid is dibasic, and phosphoric acid tribasic. There are, therefore, three phosphoric acids, which differ in the fact that one, two, or three atoms of H may be replaced by as many basic atoms. It is to Graham that we owe the discovery of their characteristic reactions. Metaphosphoric acid only forms one species of metaphosphate. Pyrophosphoric acid yields two species of pyrophosphate. Orthophosphoric acid forms three species of salts corresponding to the formulæ M_3PO_4; M_2HPO_4; MH_2PO_4. These acids are distinguished one from the other by the following reactions: the meta acid gives a white precipitate, with barium chloride also with silver nitrate, and coagulates a solution of albumen; the pyro acid gives no precipitate with barium chloride, but a white precipitate with silver nitrate, and does not coagulate albumen the ortho acid gives no precipitate with barium chloride, but a yellow precipitate with silver nitrate, and does not coagulate albumen.

Phosphoric Anhydride, P_2O_5, is obtained by the combustion of phosphorus in a current of very dry air. It forms extremely light, highly deliquescent, white flocks. It dissolves in water with the hissing noise of red-hot iron. Hence its use in drying gases at temperatures at which sulphuric acid would be decomposed, and also in the preparation by dehydration certain acid anhydrides or certain organic compounds, nitriles for example. Heated to redness with charcoal it yields carbonic oxide and phosphorus.

Metaphosphoric Acid, HPO_3, is monobasic. It is prepared by hydrating the cold anhydride, by heating orthophosphoric acid to redness, or by calcining ammonium phosphate at a red heat. It is a vitreous substance, volatile at a red heat, very soluble in water with which it combines to reproduce orthophosphoric acid. It is used to dry gases. The metaphosphates prepared by calcining monometallic orthophosphates are only partially reduced by charcoal.

Pyrophosphoric Acid, $H_4P_2O_7$ is dibasic. It is prepared by subjecting orthophosphoric acid to prolonged heat at 200° C. Calcined, it gives metaphosphoric acid; with water it reproduces orthophosphoric acid. Pyrophosphates, prepared by calcining bimetallic orthophosphates, or by heating phosphoric acid with an oxide, are reducible by charcoal.

As far as the manufacture of chemical manures is concerned, the most important modification is the ordinary or orthophosphoric acid. However, pyrophosphoric acid is sometimes met with in phosphates that have been roasted to facilitate grinding, and metaphosphoric acid in superphosphates dried at too high a temperature.

Orthophosphoric Acid, H_3PO_4.—This, the ordinary phosphoric acid, is tribasic. It is obtained mixed with phosphorus, in the slow oxidation of phosphorus in moist air. It is prepared in the laboratory by oxidizing red phosphorus by the aid of heat with fifteen times its weight of nitric acid of 20° B. The reaction may be expressed thus: $3P + 5HNO_3 + 2H_2O = 3H_3PO_4 + 5NO$. The phosphorous is added gradually and in small portions at a time. Orthophosphoric acid is produced, which remains in the retort, and nitrogen dioxide, which carries over some nitric acid. Care is therefore taken to redistil the product until the whole of the phosphorus has disappeared; the residue is then evaporated in a platinum basin to expel all nitric acid and to convert any phosphorus acid which may have been formed into phosphoric acid, taking care not to exceed 188° C., otherwise pyrophosphoric acid will be obtained. Orthophosphoric acid is also produced by the action of hot water on metaphosphoric acid, by igniting hypophosphorus or phosphorous acids, or by the action of water in excess on pentachloride of phosphorus. In the concentrated state ordinary phosphoric acid forms a thick, inodorous, very acid, non-poisonous syrup, of density 1·88. It crystallizes with three molecules of water when evaporated under a bell jar over sulphuric acid. It is very soluble in water, and highly deliquescent. Under the action of heat, it is converted at about 213° C. into pyrophosphoric acid, and towards a red heat into metaphosphoric acid. It is reduced by red-hot charcoal, yielding phosphorus. It gives no precipitate with barium chloride, with ferric chloride with a solution of silver nitrate, nor with albumen. But if ammonia be cautiously added, barium chloride gives a brownish precipitate, and a solution of silver a yellow one; both precipitates being soluble in acetic acid. A characteristic test for phosphoric acid is the production of the double phosphate of magnesium and ammonium, by "magnesia mixture," consisting of ammonia, magnesium chloride, and water. This precipitate is white and crystalline; its appearance and method of formation being very characteristic. A reagent which enables traces of phosphoric acid to be detected, consists of a nitric acid solution of ammonium molybdate. If the mixture of the two solutions be heated, a bright yellow precipitate is formed. Ordinary phosphoric acid is a very stable compound. At a high temperature it displaces sulphuric and nitric acids from their compounds.

Phosphates of Lime.—It has just been seen that phosphoric acid is tribasic, i.e. it contains three atoms of hydrogen, replaceable by metals:—

$$PO\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right. \qquad PO\left\{\begin{matrix}OM\\OH\\OH\end{matrix}\right. \qquad PO\left\{\begin{matrix}OM\\OM\\OH\end{matrix}\right. \qquad PO\left\{\begin{matrix}OM\\OM\\OM\end{matrix}\right.$$

Orthophosphoric Acid	Monometallic Orthophosphate	Dimetallic Orthophosphate	Trimetallic Orthophosphate

When the hydrogen of phosphoric acid is replaced by calcium, a divalent element, three types of phosphates are obtained to which the commercial varieties of phosphatic manures correspond in a very characteristic fashion:—

$$PO\begin{cases}OH\\OH\\O\end{cases}\!\!>Ca \qquad\qquad PO\begin{cases}O\\O\end{cases}\!\!>Ca \qquad\qquad PO\begin{cases}O\\O\end{cases}\!\!>Ca$$
$$PO\begin{cases}O\\OH\\OH\end{cases} \qquad\qquad\quad \begin{matrix}O\\O\end{matrix}\!\!>Ca \qquad\qquad\quad \begin{matrix}O\\O\end{matrix}\!\!>Ca$$
$$\qquad\qquad\qquad\qquad PO\begin{cases}OH\\OH\end{cases} \qquad\qquad PO\begin{cases}O\\O\end{cases}\!\!>Ca$$

Monocalcic phosphate or acid phosphate of lime, $CaH_4(PO_4)_2$	Dicalcic phosphate or monacid phosphate of lime	Tricalcic phosphate, Neutral phosphate of lime, Tribasic phosphate of lime, $Ca_3(PO_4)_2$

Monocalcic phosphate or superphosphate is characterized by its complete solubility (*a*) in water, (*b*) in ammoniacal citrate of ammonia (aqueous solution of ammonium citrate with excess of ammonia), and (*c*) in mineral acids. The sole object of superphosphate manufacture is to convert the tricalcic phosphates of bones and mineral phosphates into monocalcic or acid phosphate, assimilable by plants. Dicalcic phosphate, or precipitated phosphate, is insoluble in water, but soluble in ammoniacal citrate of ammonia, and mineral acids. It is obtained in the treatment of bones by hydrochloric acid, in the manufacture of gelatine (glue), as will be seen in the sequel. Tricalcic phosphate forms the chief mass of the substance of bones which resists combustion (bone ash), of phosphorites, of apatite, and of a great number of guanos. In the calcined state, or as apatite, it is insoluble in water, slightly soluble in water saturated with carbonic acid. It is completely soluble in nitric and hydrochloric acids, which convert it into monocalcic phosphate, displacing two-thirds of the lime to form, with it, calcium nitrate or calcium chloride. Sulphuric acid completely decomposes it into free phosphoric acid and sulphate of lime (gypsum). Phosphoric acid is precipitated from acid solutions, by excess of lime water, as a fine white powder, which is partly soluble in water, especially when it contains potassium sulphate, common salt, nitrate of soda, ammoniacal salts, or carbonic acid.

Phosphates of Ammonium, Sodium, etc.—Let us examine a few other phosphates of importance in manure manufacture:—

1. *Tribasic Phosphate of Ammonium*, $(NH_4)_3PO_4$, is a slightly soluble, very unstable salt, obtained by mixing syrupy phosphoric acid with excess of ammonia. Its aqueous solution exposed to the air loses one-third of its ammonia, and is converted into the monacid phosphate; heated, it loses a second equivalent, and is then converted into the acid phosphate.

2. *Monacid Phosphate of Sodium (ordinary commercial phosphate of soda,* $Na_2HPO_4 + 12H_2O$) is contained in urine. It forms

large crystals, which become opaque in the air, through loss of a portion of their water. Heat converts it into pyrophosphate by expulsion of water. It is prepared on the large scale by saturating crude phosphoric acid with soda to alkaline reaction and crystallizing.

3. *Monacid Phosphate of Ammonium and Sodium*, $NaNH_4HPO_4 + 4H_2O$.—This salt is prepared by dissolving ammonium chloride in a solution of ordinary phosphate of soda. Heat converts it into sodium metaphosphate, $NaPO_3$, with liberation of ammonia and water. Putrefying human urine yields a deposit of this salt. It forms crystals as clear as water, and is found in that state in guano, under the name of *stercorite*. Its solution on standing gives off ammonia.

4. *Monacid Phosphate of Ammonium* is, likewise, found in Peruvian guano. It is formed from the neutral salt through loss of ammonia. It has an alkaline reaction, like all monacid soluble phosphates. The acid phosphates of potassium, of sodium and of ammonium are still more soluble in water than the preceding. Their solutions turn red litmus paper blue.

5. *Magnesium Phosphates*—(1) *Basic Phosphate of Magnesium* $Mg_3(PO_4)_2$, is found in small quantities in seeds. It is very soluble in acids; it is precipitated from its acid solution by ammonia as phosphate of ammonia and magnesia. (2) *Monacid Phosphate of Magnesium.*—This, like the corresponding lime compound, is a very soluble salt. (3) *Double Phosphate of Ammonium and Magnesium*, $NH_4MgPO_4 + 6H_2O$, is precipitated from solutions which contain at one and the same time phosphoric acid, magnesia salts and ammonia, as a white crystalline powder slightly soluble in water and almost insoluble in ammonia water. Ignited, it leaves a residue of pyrophosphate. This interesting compound was found in large crystals as clear as water in excavating the soil for the foundations of the church of St. Nicolas in Hamburg. The name of *struvite* was given to it. In this locality there was a cesspool, from which the matter spread into the peaty soil. As peat contains a large amount of ammoniacal salts, the phosphate of magnesia from the urine had formed the double phosphate of ammonia and magnesia, which remained in solution for a somewhat lengthened period in the ammoniacal salts in excess. By slow precipitation crystals were formed, some as large as a hazel nut. This same salt is met with in different varieties of guanos, but in much smaller crystals. Its formation is analogous to that which occurs in putrefying urine: the phosphate of magnesia is brought by the urine, the ammonia results from the putrefaction of the nitrogenous constituents of the guano.

6. *Phosphates of Iron.*—The basic phosphates of iron are widely distributed in nature, but their composition is very variable. They are formed wherever phosphates dissolved by the moisture

in the soil come into contact with oxide of iron. In arable land, which it is well known always contains oxide of iron, a portion of the phosphoric acid is in all probability combined with that oxide. The phosphate of the protoxide of iron (ferrous phosphate) is formed in an analogous manner, in nature the iron reduced to protoxide by decomposing organic matter. This product is found in large masses in certain peaty districts. A basic artificial phosphate is obtained by mixing ferric chloride with excess of phosphate of soda. It possesses a yellowish colour, but becomes brown on heating. The compound so obtained is never pure, and its composition in no case corresponds to definite proportions. The pure basic phosphate is obtained from the preceding by moistening it with pure syrupy phosphoric acid, and washing it with a great excess of water. The product so obtained remains white on ignition. It is soluble in hydrochloric acid, ferric chloride, and in acetate of iron, but insoluble in acetic acid. The acid phosphate of iron is prepared by dissolving the freshly precipitated, air-dried, basic phosphate in pure, syrupy phosphoric acid. Properly prepared, and the water abstracted, the solution has an analogous composition to other acid phosphates; it is rose-red, and may be converted by means of a large excess of water into free phosphoric acid and basic phosphate. It likewise yields a precipitate on heating. Tartaric, citric, and other non-volatile organic acids prevent the formation of the precipitate; mineral acids only possess this property but imperfectly.

7. *The Phosphates of Alumina* behave in a general way like the phosphates of iron. Wavellite, a crystallized mineral phosphate, is a phosphate of alumina. Redonda phosphate, which forms an important deposit, consists chiefly of a compound of this nature.

The phosphates just described are met with in different phosphatic manures, natural or artificial. The majority of them, such as the alkaline and ammonium phosphates, are only represented in small proportions it is true; however, one cannot but acknowledge their vast importance from the point of view of the mobility of phosphoric acid in the soil, and in the organism. The only phosphates found in preponderating amount in manures are the phosphates of lime. The tribasic phosphates of lime are spread over numerous points of the globe; as will be seen further on considerable deposits of them exist which are worked commercially. But these phosphates are mixed with more or less impurities, owing to their abundance they serve exclusively as raw material for the manufacture of phosphatic manures, properly so called, which are acid phosphates of lime, or *superphosphates*.

Moreover, various industries supply important quantities of basic phosphates, obtained as bye-products. These are delivered to manure manufacturers, who use them in making superphosphates, or they are dispatched direct to the farmers (basic slag).

CHAPTER II.

PRINCIPAL PHOSPHATE DEPOSITS.

I. FRANCE.—*Pas de Calais, Somme, Oise.*—In these departments the deposits of phosphates are met with in the Cretaceous formation, at three distinct levels. These are in ascending order. 1. The Gault to which the Boulogne workings belong. The nodules found in these beds contain 20 per cent of phosphoric acid. 2. The Glauconian chalk, which forms the phosphate basin of Pernes and of Fauquemberg, with 25 per cent of phosphoric acid. 3. The Upper Chalk bed, characterized by *Belemnites quadratus*, the most important of all. The phosphate deposits of Orville, Beauval, and Hardivillers are on this horizon. In these workings phosphate rich in sand is found in pockets, in the upper chalk, below the clay or surface *bief* (? boulder clay). These pockets, which are wrought very energetically, are only of limited duration, and are in process of exhaustion. Besides the pockets of rich sand, there exist in the *Belemnites* chalk cliffs parts sufficiently rich in phosphate of lime to be worth extracting and treating by one of the enrichment processes to be described further on. This phosphatic chalk, called also "grey chalk" (*craie tuffeau*), etc., forms in certain points masses of considerable dimensions. The percentage does not exceed 38 to 40 of tribasic phosphate of lime. Below 28 or 30 per cent of tribasic phosphate of lime, the chalks are mostly considered as of no industrial value. At Breteuil near Clermont, for example, an extremely important bed of this chalk with 32 per cent of tribasic phosphate is only partially exploited, the enriched product not exceeding 45 per cent of tribasic phosphate.

1. *Somme Phosphate.*—The presence of phosphatic chalk in the Somme was first observed by Buteaux as far back as 1849. On the other hand, M. de Mercy discovered in 1863 and 1867 two other similar deposits, the one at Hardivillers near Breteuil (Oise), the other at Hallencourt near Abbeville, Somme; he showed their analogy with that of Beauval, and classed them along with the latter as belonging to the *Belemnites quadratus* chalk. The Beauval deposits were discovered in 1886 by two geologists, Merle and Poncin. The phosphatic sands of that locality, and its environs, are accumulated on the edges of pockets in the form of reversed cones excavated in a bed of chalk, filled with small brown-yellow grains of phosphate of lime situated at the base of the *Belemnites quadratus* chalk, and resting on the *Micraster Coranguinum* white chalk. This formation is found therefore about the middle Senonian horizon. The

phosphatic chalk is of a bright chamois colour and is known in the district under the name of grey chalk; its phosphoric acid content is from 10 to 15 per cent at the point of contact of the grey chalk and the white, *Micraster*, chalk. There is at Orville a discontinuous, almost horizontal bed of phosphatic nodules of a yellowish-white colour. Some are coloured black on the exterior, due to a bright coat which would appear to be manganese dioxide; they are rarely the size of a small nut and contain 70 to 80 per cent of tribasic phosphate. They are agglomerated by a gangue of white carbonate of lime. The phosphatic sands of the Somme contain a rather large quantity of the teeth of dogfish, which appear to have been preserved by their enamel. Neither fossils nor bones are found there, though they exist in the *Belemnites* chalk. At Orville, where the phosphatic chalk is separated from the *Micraster* chalk by a bed of nodules, no nodules come from this bed except from the bottom of pockets which descend below the grey chalk. At Beauval, where the bed of nodules is absent, there is only to be seen at the apex of the funnels granular hard parts somewhat rich in phosphoric acid. The amount of rich phosphatic sand in the deposits of the neighbourhood of Doullens, including that of Orville, which though situated in the department of the Pas de Calais ought to be considered as belonging geologically and commercially to the Somme group, has been estimated at about 1,500,000 tons. But these deposits are on the road to exhaustion. Soon, as Olry remarks, this region will re-enter the calm of olden times, and of this era of untold riches, beyond the fortunes acquired by certain privileged persons, there will only remain the memory aggrandized by tradition of a time of fever and of gain almost unique in French industrial annals. Some analyses of the phosphates of these deposits are now given.

TABLE II.—ANALYSES OF THREE DIFFERENT TYPES OF SOMME PHOSPHATES.

	75-80 Per cent Phosphate.	70-75 Per cent Phosphate.	60-65 Per cent Phosphate.
Moisture at 100° C.	0·59	1·42	2·80
Organic matter and combined water	1·43	—	—
Phosphoric acid	35·59	34·10	29·10
Lime	51·02	50·01	41·23
Oxide of iron	0·83	1·30	4·07
Oxide of alumina	0·56	0·23	
Magnesia and carbonic acid	9·17	—	CO_2 3·05
Insoluble in acids	0·79	1·60	8·55
Equal to tribasic phosphate of lime	77·69	74·44	63·53

TABLE III.—ANALYSIS OF AVERAGE SAMPLE FROM A FIELD OF ORVILLE PHOSPHATE DRIED IN VACUO AT 98° C. DENSITY AT 16° C. 3·1307. (H. LASNE.)

	Per cent.
Sand and clay insoluble in hydrochloric acid	1·36
Organic matter and water volatile at a red heat	3·40
Soluble silica	0·47
Carbonic acid	3·70
Sulphuric acid (SO_3)	0·75
Phosphoric acid	33·86
Lime	47·54
Magnesia	1·20
Alumina	1·70
Oxide of iron (Fe_2O_3)	1·22
Calcium fluoride	4·65
	99·85

TABLE IV.—BEAUVAL PHOSPHATE DEPOSIT. ANALYSIS MADE BY NANTIER AT THE DATE OF DISCOVERY.

	Per cent.
Phosphoric acid	30·89
Lime	45·33
Carbonic acid	2·04
Fluorine	1·60
Sulphuric acid	1·84
Peroxide of iron	0·50
Alumina	0·32
Magnesia	0·16
Silica	0·38
Organic matter	2·26
Water	15·99
	101·31

Which corresponds before drying to a content of—

Phosphate of lime	67·43
Carbonate of lime	4·60
Calcium fluoride	3·24
,, sulphate	1·43

Drying raises the phosphate of lime content of this product to 80 per cent.

2. *Pas de Calais Phosphates.*—The phosphate bed situated between the Gault and the Greensand extends over vast tracts. In the Pas de Calais it forms the prolongation of deposits recognized in England as of the same stratigraphical horizon in the counties of Kent, Sussex, and Surrey. There is reason also to assimilate it with the geological horizon exploited in the Ardennes and in the Meuse. It was in the Pas de Calais at Wissant that Berthier first

discovered in France the presence of phosphate of lime in nodules, amongst pyrites being wrought at the base of the Gault clay for the manufacture of green vitriol. The stony matter mixed with the pyrites yielded on analysis 57·4 per cent of phosphate of lime. Later on, Dr. Turner discovered phosphatic nodules in the Gault at Lottinghem. Finally, the investigations of Meugy, Desailly, and de Molon in the Ardennes, from 1852 to 1856, having drawn public attention to the phosphates of the Greensand, these were not long in being exploited in the Pas de Calais, which has since become one of the principal centres of production. The nodules or lumps of this bed to which the name of *coquins* are still given, are generally round in form smooth or mamillary. Their size varies from that of a nut to that of the fist. They are grey or brown on the surface, with sometimes a bluish, sometimes a greenish cast. In the interior they are dark brown or black. Some of them are penetrated by iron pyrites, glauconite, gypsum, or quartz. In the Pas de Calais they are consolidated by an argillaceous cement containing 25 per cent of glauconitic sand, which makes a sort of conglomerate, of which the mass is formed of 35 to 40 per cent of nodules, and 60 to 65 per cent of argillo-silicious matter; sometimes shells, woody fragments, coniferous fruits, dog-fish teeth, fish bones, and crystals of carbonate of lime, are found therein. The bed of nodules is fairly regular; its thickness varies from 6 to 8 inches.

Chemical Composition of the Pas de Calais Nodules.—The chemical composition of the nodules varies, as two analyses by Delattre show.[1] It follows from these analyses that the Gault nodules consist essentially in the Pas de Calais of phosphate of lime, carbonate of lime, fluoride of calcium, clay, sand and glauconite, the whole associated with a certain proportion of organic matter, about 0·10 per cent of nitrogen (ammoniacal); the glauconite brings also a certain amount of potash. The extent believed to be exploitable in the bed situated at the base of the Gault clay is estimated at 600 hectares, say 1500 acres, in the Boulogne district. At the base of the Cenomanien formation or Glauconitic chalk, there are in certain localities in the Pas de Calais workable beds of phosphate of lime. Also, in the district of Audincthem, Dennebrœucq and Reclinghem, and in that of Fléchin, Febvin-Palfart, Nédonchelle, Bailleul-les-Pernes, Aumerval and Pernes-en-Artois, at a short distance from the coal basin. The bed of phosphate has a thickness of 5 to 10 inches; the nodules are greenish, rather large and agglomerated by a sandy clay. They are more friable than those of the Boulogne district, and yield, on washing, about 25 per cent of by-products. They contain from 50 to 60 per cent of phosphate of lime.

[1] See Table V, p. 18.

TABLE V.—ANALYSES OF PAS DE CALAIS PHOSPHATES.

	Phosphate. Nabringhem.	Phosphate. Fiennes.
Moisture at 100° C.	1·40	1·40
Matter volatile at a dull red heat	5·60	5·30
Phosphoric acid (1)	23·52	20·72
Sulphuric acid	1·06	0·89
Carbonic acid (2)	4·30	4·20
Fluorine (3)	1·90	1·83
Lime	34·77	33·71
Magnesia	0·04	traces
Alumina	3·53	3·25
Oxide of iron	3·19	3·15
Silica	20·60	25·20
	99·91	99·65
Deduct oxygen equal to the fluorine	0·80	0·77
	99·11	98·88
Undetermined and loss	0·89	1·12
Total	100·00	100·00
(1) Equal to tribasic phosphate of lime	51·36	45·23
(2) Equal to carbonate of lime	9·77	9·54
(3) Equal to calcium fluoride	3·90	3·76

3. *Meuse, Ardennes and La Marne Phosphates.*—The phosphates exploited in this district come almost entirely from the base of the cretaceous (Greensand). This formation forms almost a continuous zone which extends over 187 miles from the department of Ardennes as far as Yonne, crossing those of la Meuse, la Marne, and the Haute Marne and Aube. It consists mostly of one, sometimes of two beds of nodules of phosphate of lime, of a thickness of 6 to 8 inches, but in certain districts it thins out so much as to be no longer workable, the phosphate disappearing entirely, or not existing in sufficient quantity. The existence of Greensand nodules in *les Ardennes* was first pointed out in 1842 by Sauvage and Bauvignier, and their chemical composition was determined in 1852 and 1853 by Meugy. The first extraction works were undertaken by Desailly in 1856 and are still in existence. But, in a general way, the works are very unstable, the sheds being removed as soon as the dead ground becomes too powerful, or the nodule bed thins out. The Meuse nodules have much the same appearance and composition as those of the Boulogne district; their phosphoric acid content generally varies from 14 to 20 per cent; it rarely exceeds the latter limit. Sometimes they are small, sometimes they reach or exceed the size of an ostrich's egg; they exhibit irregular contours into the spaces between which a green argillaceous sand penetrates, which necessitates their being broken in bulk so as to clean them. At other times the phosphate of lime instead of being in lumps isolated in the sand assumes the form of a conglomerate

with a sandy cement known under the name of *Crassins*. These Crassins are very difficult to clean. and yield products poor in phosphoric acid. A sample of nodules from the neighbourhood of Grandpré, analysed at the *Bureau d'Essais de l'École des Mines*, had the following composition :—

TABLE VI.—ANALYSIS OF MEUSE PHOSPHATES.

	Per cent.
Clay and quartz	14·0
Alumina and oxide of iron	25·5
Lime	32·5
Phosphoric acid	17·5
Carbonic acid	9·0
Total	98·5

Other and more complete analyses have been published by Delattre. The following are quoted :—

TABLE VII.—ANALYSES OF VARIOUS PHOSPHATES IN THE MEUSE, ARDENNES, ETC., DISTRICTS. (DELATTRE.)

	Source of the Phosphates.			
	Les Islettis.	Dombasle.	Grandpré.	Chesnors or Boncourt.
Moisture at 100° C.	1·90	1·75	2·20	2·15
Matter volatile at a red heat	5·05	4·80	4·55	3·75
Phosphoric acid	18·74	18·23	19·57	16·69
Sulphuric acid	1·20	0·79	0·85	0·79
Carbonic acid	4·80	4·50	5·80	4·70
Fluorine	1·48	1·31	1·66	1·75
Lime	29·23	27·66	31·81	26·88
Magnesia	0·39	traces	0·36	traces
Alumina	2·57	2·30	3·36	2·47
Oxide of iron	5·46	5·83	4·89	3·77
Silica	28·74	32·06	24·80	37·16
	99·56	99·23	99·95	100·11
Deduct oxygen equal to fluorine	0·62	0·55	0·69	0·75
	98·94	98·68	99·16	99·36
Undetermined and loss	1·06	1·32	0·84	0·62
Totals	100·00	100·00	100·00	100·00
Equal to phosphate of lime	40·90	39·79	42·73	36·43
Equal to carbonate of lime	10·90	10·23	13·18	10·68
Equal to calcium fluoride	3·05	2·70	3·40	3·59

TABLE VIII.—ANALYSIS OF ARDENNES NODULES. (MARET AND DELATTRE.)

	Per cent.
Moisture	2·20
Organic matter	3·35
Carbonic acid	4·60
Sulphuric acid	0·75
Phosphoric acid	18·35
Fluorine	1·37
Lime	27·52
Magnesia	0·08
Alumina	2·37
Oxide of iron	5·20
Potash soluble in nitric acid	0·99
Silica	32·42
	99·20
Deduct oxygen equal to fluorine	0·57
	98·63
Undetermined and loss	1·37
	100·00
Carbonate of lime	10·45
Phosphate of lime	40·08
Calcium fluoride	2·81
Nitrogen	0 084

These analyses show that the Meuse and Ardennes nodules are similar in composition to those of Boulonnais and the neighbourhood of Pernes-en-Artois, which is quite natural, both being of the same origin and situated at almost the same geological horizon.

4. *Côte d'Or Phosphates.*—As far back as 1822, De Bonnard discovered near St. Thibault (Côte d'Or), in a cutting of the Burgundy Canal, greyish-white nodules which contained, according to an analysis by Berthier, 74 per cent of phosphate of lime. These nodules associated with grains of ammonite were impasted in a mass of brown clay, but at that period little importance was attached to the discovery, and it was only in 1872 that Collenot re-discovered them in excavations made on the line of the railway from Oravant to Laumes. He collected samples which Georges Ville found to contain 60 to 64 per cent of tribasic phosphate. In 1873-4 this formation was examined by Poncin, who immediately profited thereby. It was thus that towards the end of 1876 the phosphate works of Auxois came into being. The horizon exploited belongs to the Lower Lias of Burgundy; it is situated towards the summit of the gryphesis *arquées* (? gryphea incurva) limestone zone with *Ammonites Stellaris.* Towards the top this limestone is rich in soft, almost friable phosphatic nodules, which are enclosed in the marly mass, the whole forming a mixture, the phosphate content of which varies from 30 to 45 per cent. The phosphatic

limestone is known in the district as "calf's liver" (*foie de veau*). It is not workable in the natural state owing to its irregular composition, but over large stretches the gryphea limestone has been altered and dissolved by the surface water which has left in *in situ*, as an insoluble residue, an argillo-ferruginous mud in which the phosphate bed is represented by a layer of nodules cemented by a gangue of a similar nature. In such conditions the phosphate nodules may be exploited, for it is easy to separate them from the substance with which they are mixed, by drying and sorting, followed by washing. The thickness of the bed varies from 10 to 20 cm. (4 to 8 inches), but this thickness sometimes reaches 30 and even 40 cm. (12 to 16 inches), whilst elsewhere the bed is lost completely and ceases to be exploitable. The nodules are irregular in shape and greyish-white or yellowish; they are soft, almost friable. Their fracture shows grey spots with some blackish veins. Their size varies from that of a hazel nut to that of the fist. They generally have rounded edges, exhibiting a more or less angular shape. The

TABLE IX.—ANALYSES OF AUXOIS PHOSPHATES. (DELATTRE.)

	I. Per cent.	II. Per cent.	III. Per cent.
Water at 100	2·10	1·60	1·20
Matter volatile at a red heat	2·10	2·50	2·50
Phosphoric acid	27·06	28·89	29·71
Sulphuric acid	traces	0·17	0·17
Carbonic acid	2·60	2·50	2·20
Fluorine	1·75	2·40	1·55
Lime	35·81	37·92	38·08
Magnesia	traces	0·18	traces
Alumina	2·40	2·47	2·63
Oxide of iron	7·35	7·24	7·45
Silica	18·30	14·40	14·20
	99·20	99·97	99·69
Deduct oxygen equal to the fluorine	0·75	1·01	0·65
	98·47	98·96	99·04
Undetermined matter and loss	1·53	1·04	0·96
Totals	100·00	100·00	100·00
Equal to phosphate of lime	59·07	62·41	64·85
Equal to carbonate of lime	5·90	5·68	5·00
Equal to calcium fluoride	3·59	4·94	3·16

mass contains 20 to 25 per cent of nodules, and 75 to 80 per cent of mud. The thickness of the mud or clinker which covers the bed is very variable, ½ to 3 metres (20 to 120 inches) at the most. The Auxois nodules contain 27 to 30 per cent of phosphoric acid, equal to 59 to 65 per cent of tribasic phosphate of lime. The results of three analyses by Delattre are given in Table IX (see previous page).

According to the French mining statistics of 1887, the approximate extent of the Côte d'Or phosphate deposits is estimated at 5000 hectares (12,500 acres), containing 1,500,000 tons of that product.

5. *Cher Phosphate.*—Beyond the districts described, a bed with nodules 15 cm. to 20 cm., say 6 to 8 inches thick, situated in the upper Albian, has lately been wrought in the department of Cher. These nodules, of a yellowish-white colour and sometimes loaded with silica, are associated with white quartzose sand and gravels in the proportion of about one-third. They contain only 14 to 16 per cent of phosphoric acid. They are hard, and hence difficult to grind, and their freight was heavy owing to the great distance from a railway station. They were wrought exclusively in the open air, within the radius of Vailly sur Saldre, then after having been washed on the spot, they were ground and dispatched. The irregularity of the deposit, the poor phosphoric acid content of the nodules, their great hardness and the heavy cost of freight, rendered these workings expensive, and they were abandoned.

6. *Quercy Phosphates (Lot and Neighbouring Departments).*—Phosphate deposits occur over a wide area in Quercy. The phosphate occurs in concretions in the form of big pockets or vertical veins in the limestone (*causses*) belonging to the lower oligocene. They are found only in the high limestone plateaus which have been traversed by the fresh waters of the eocene, and almost always in the immediate neighbourhood of tertiary *ilots* (outliers) left on the spot. These outliers never exceed 350 metres (1148 feet) high, and it would be useless to seek for phosphate pockets on Jurassic plateaus of greater altitude. The pockets are very variable; some have a diameter of 35 metres (115 feet), others are crevasses of 3 to 6 metres (10 to 20 feet), following a straight line over 90 metres (say 300 feet). All the known pockets end in a point at the bottom, and widen near the surface. The irregular nature of these deposits seems to form an obstacle to their development. Their high phosphoric acid content apparently led to a multiplication of badly organized works which ceased to be self-supporting when it was necessary to go deeper. These phosphates are chiefly used in the manufacture of superphosphates to increase the percentage of phosphates, so as to bring them to the commercial standard of 15 to 16 per cent of phosphoric acid soluble in ammonium citrate. Their average composition is as follows:—

TABLE X.—ANALYSIS OF QUERCY PHOSPHATES.

	Per cent.
Water and organic matter	5·31
Phosphoric acid	35·33
Lime	48·72
Carbonic acid	3·42
Sulphuric acid	—
Fluorine	—
Magnesia	0·08
Oxide of iron	2·24
Alumina	2·78
Insoluble	2·12
	100·00

7. *Gard and Ardeche Phosphates.*—The Gard deposits are chiefly phosphorites, the formation of which has been contemporaneous with those of Quercy. They are found in irregular excavations amongst the compact limestone of the Urgonian age. The workings are underground. The chief producing centres are on the lands of the communes of Tavel and Lirac. There are also deposits of nodules in Saint-Julien-de-Peyrolas and Salazac, also in the department of Ardeche at Saut-de-l'Eygue, la Rousette, Beyne, etc. Production almost nil.

8. *Drôme and Isère Phosphates.*—In Drôme they chiefly work the Greensand nodules at Saint-Paul-Trois-Chateaux in the district of Montelimar. The content of these nodules does not exceed 55 per cent of tribasic phosphate of lime; it averages 45 per cent. The workings, which are unimportant, are solely in the open air, and consist of screening the nodules and scrubbing them in water to separate adhering sand. In Isère there are fossiliferous and phosphatic beds (Gault) of great regularity, but the rock is sometimes so compact that the nodules cannot be washed and enriched by simple economic means, such as screening and scrubbing, which are the only methods that can be applied to material so poor in value.

9. *Pyrenees or Arièges Phosphates.*—These phosphates, described by Dr. Levat in a memoir presented to the Academy of Sciences, form a vast bed developed in the valleys of Bonnes, Luchon, Salat, in the neighbourhood of Prades, ascending towards the north in les Corbières as far as the environs of Cannes. Pyrenees or Arièges phosphates have a brilliant black appearance recalling that of anthracite. The composition of the bed is characterized in its rich parts by numerous black, brilliant, usually flattened nodules consisting of almost pure phosphate of lime, testing 65 to 75 per cent of tribasic phosphate of lime. The gangue encrusting these nodules is itself phosphatic. Moreover, there has been found in it an important amount of organic matter containing organic nitrogen in the proportion of 11 lb. per ton. The thickness of the bed reaches 8 to 10

metres (26 to 33 feet). The nodules are concentrated sometimes on the roof, sometimes on the wall of the deposit.

II. BELGIUM.—About 1874, Cornet discovered at Mesvin and at Ciply near Mons, below the landenien sands, a bed 8 to 10 metres thick of brownish, friable, slightly coherent chalk containing 75 per cent of brown grains of carbonate and phosphate of lime, the largest of which are not bigger than a pin's head. This speckled chalk, known in the district as brown chalk (*craie brune*), contains 25 to 30 per cent of tribasic phosphate, with a slight enrichment at the base. It occurs at a higher level than the Beauval chalk. In the upper part it exhibits pockets, in which there are found masses of pudding-stone called *poudingue de la Malogne*, consisting of brown coloured nodules containing 50 per cent of phosphate, cemented together by a calcareous paste. These nodules have an analogous composition with the brown grains. The calcareous tufa of Maestricht, itself phosphatic, rests on them. Other pockets, containing a chestnut-coloured phosphatic sand, like a highly ferruginous sand, tests 60 per cent of tribasic phosphate. This sand, which coats the sides of the excavations, is only about 30 cm., say 12 inches thick. It consists of the same small phosphatic grains that are met with in the brown chalk. The phosphatic chalk of Mesvin and Ciply, like that of Somme, is not commercially utilizable in its raw state, but its extreme friability, and the facility with which the phosphatic grains are detachable from their chalky envelope, enable it to be enriched and to bring its content up to 50 and even 60 per cent of phosphate. It suffices to pulverize it and to submit it afterwards to an ascending current of air which removes the chalk dust

TABLE XI.—ANALYSES OF CIPLY PHOSPHATES.

	I.	II.	III.	IV.
Water	0·65	0·30	—	1·40
Organic matter	3·00	2·50	2·12	1·90
Phosphoric acid	18·68	22·14	24·69	26·29
Sulphuric acid	0·01	—	—	1·61
Lime	49·90	50·72	50·31	51·98
Carbonic acid	18·40	15·70	15·06	12·80
Magnesia	0·59	—	—	0·67
Oxide of iron and alumina	2·28	1·72	1·31	0·86
Insoluble	5·20	3·30	1·23	0·74
Undetermined	1·29	3·62	5·28	1·75
Totals	100·00	100 00	100·00	100·00
Equal to tribasic phosphate of lime	40·72	48·25	53·82	57·39
Equal to carbonate of lime	41·81	35·64	34·24	29·09

and leaves the small heavier phosphatic grains, or to roast it slightly and to wash it in mechanical preparation plant. Other important phosphatic deposits occur in the district of Liége, at Rocour, Vottem, Hesbaye, on the right bank of the Meuse. It likewise occurs at Liers, Voroux, Milmort, Ans and Montéguée.

TABLE XII.—ANALYSES OF LIÉGE PHOSPHATES.

	I. Per cent.	II. Per cent.
Water	0·93	0·85
Chemically combined water	2·83	2·53
Phosphoric acid	27·20	25·08
Carbonic acid	3·10	3·00
Soluble silica	0·80	0·75
Lime	40·64	38·01
Magnesia	0·79	0·81
Oxide of iron and alumina	2·39	3·30
Calcium fluoride, calcium sulphate, etc.	5·93	4·40
Insoluble	15·34	21·27

III. England.—True coprolites or fossil excrements rich in phosphate of lime in the form of more or less rounded lumps, 6 to 20 cm. (2½ to 8 inches) in diameter, are found in England in the Lias marls, chiefly at Lyme Regis. The interior is earthy like hardened clay, but amongst these there can be readily distinguished the teeth and the bones of the fishes and reptiles which served as food to the saurians of the epoch such as the ichthyosaurus, the pleiosaurus and the teleosaurus. Coprolites have been found at the mouth of the Severn near Bristol.

TABLE XIII.—ANALYSES OF LYME REGIS COPROLITES. (THOMPSON HERAPATH.)

	I. Per cent.	II. Per cent.
Water	6·182 (Water and organic matter)	2·976
Organic matter		2·001
Sodium chloride and sulphate	traces	—
Carbonate of lime	23·674	28·121
Carbonate of magnesia	—	0·423
Sulphate of lime	1·077	0·026
Phosphate of lime	60·769 (with phosphate of magnesia)	53·996
Phosphate of magnesia	traces	
Phosphate of iron	4·057	6·182
Phosphate of alumina	traces	4·276
Ferric oxide	1·994	—
Alumina	traces	—
Silica, calcium fluoride, and loss	1·552	0·738
	99·305	95·739
Nitrogen	0·082	
Density	2·700	

TABLE XIV.—ANALYSES OF CAMBRIDGE COPROLITES.

	Per cent.
Moisture	8·00
Organic matter	3·00
Silica	9·00
Phosphate of lime	77·70
Carbonate of lime	2·30
	100·00

TABLE XV.—ANALYSIS OF SUFFOLK COPROLITES.

	Per cent.
Combined water	10·00
Sand, oxide of iron	21·00
Carbonate of lime	10·00
Phosphate of lime	56·00
Calcium fluoride, sulphates and alkaline chlorides	3·00
	100·00

As far back as 1848 antediluvian bones were dug out of the Suffolk and Norfolk *Crag*. The upper Norfolk Crag contains fossil bones of the elephant, rhinoceros, ox, etc. They are found mixed with sand and gravel at a depth of 70 to 80 cm. (27 to 31 inches). The samples from the bone bed in the neighbourhood of Sutton (Suffolk) are sometimes spongy and friable, sometimes fibrous and resistant. The latter readily take a fine polish, and their porosity can only be seen under the microscope. Their analysis gives the following figures:—

TABLE XVI.—ANALYSES OF FOSSIL BONES FROM SUTTON BONE BED.

	I. Per cent.	II. Per cent.
Water extracted at 150° C. to 170° C.	3·361	2·912
Water and organic matter volatile at a red heat	4·351	3·361
Carbonate of lime	27·400	26·800
Carbonate of magnesia	0·371	0·286
Sulphate of lime	0·514	traces
Phosphate of lime combined with a little phosphate of magnesia	49·632	59·966
Phosphate of iron	6·600	4·800
Phosphate of alumina	3·400	4·638
Calcium fluoride	3·617	undetermined
Silica	0·626	0·098
	99·872	99·861
Nitrogen in 100 parts	0·1244	undetermined

Two other samples from the same locality intended for superphosphate manufacture, yielded 58·61 and 62 per cent of tribasic

phosphate of lime. Besides these deposits of phosphorites, resulting from the burying of bones, phosphorites are also found in the county of Suffolk, at Felixtowe, Sutton and Walton; these deposits are 20 inches deep. The phosphorites occur there as brilliant black nodules, exceedingly hard, and were formerly used as pebbles for road-making. Their composition is as follows

TABLE XVII.—ANALYSES OF SUFFOLK, ETC., COPROLITES.

	Per cent.	Per cent.
Water and organic matter	4·0	—
Tricalcic phosphate	70·9	54
Carbonate of lime	10·28	10
Silica	5·79	—
Oxide of iron	—	5
Oxide of alumina	—	4
Fluorine	—	3

Finally, deposits of pseudo coprolites are found in the Welsh Cambrian and Silurian systems at Mowdry, Pennyganedd, and at Beroin. But the English superphosphate industry has almost entirely ceased, owing to the competition of other countries that possess more readily workable deposits. (See Table, p. 54.)

IV. SWEDEN AND NORWAY.—*Sweden.* Apatite with 36 to 41 per cent P_2O_5 is found in quartz at Horesjobera.

Norway.—In the Kragero schists, near Christiania, likewise in the granite and gneiss, crystalline appatite is met with although rarely in crystals. Its colour is yellowish-white or greenish-grey or red. The crystals have the following composition:—

TABLE XVIII.—ANALYSIS OF NORWEGIAN APATITE (CRYSTALS).

	Per cent.	
Water	0·14	
Loss on ignition	0·27	
Phosphoric acid	39·44	$= 86·10\ Ca_3P_2O_8$.
Lime	50·90	of which 2·28 is free lime.
Magnesia	0·64	
Oxide of iron	0·51	
Oxide of alumina	0·86	
Carbonic acid	0·15	
Sulphuric acid	0·12	
Chlorine	2·62	
Insoluble	3·62	

V. GERMANY.—Germany possesses practically no deposits of phosphate of lime industrially utilizable, and the recent geological examinations that have been made have yielded practically no discoveries.

VI. AUSTRIA-HUNGARY.—Deposits of poor phosphates exist in

Bohemia, at Kostic and at Teplitz, the composition of which is as follows:—

TABLE XIX.—ANALYSIS OF BOHEMIAN PHOSPHATES.

	Per cent.
Phosphoric acid	15·15
Lime	32·62
Carbonic acid	12·95
Sulphuric acid	0·82
Calcium fluoride	3·51
Magnesia	1·04
Oxides of iron and alumina	5·17
Silica	2·14
Sand	26·14

Moreover, vast deposits of phosphorite are found in Galicia and Bukovina, which are connected with those of Central Russia, as will be seen further on.

VII. Russia.—There are two deposits of phosphorite in Russia of considerable extent, one of which, part of Podolia, 500,000 hectares (1,250,000 acres), and of Bessarabia, 70,000 hectares (175,000 acres), extends into Austria. Its most important centre is in the basin of the Dneister, between St. Urzica and Nozileu. The phosphorite is found as nodules with a smooth and polished surface, rarely rugose or exfoliated, sometimes greasy to the touch and resembling polished cast-iron, 2 to 2½ inches in diameter; some are 8 inches in diameter. Their composition is as follows:—

TABLE XX.—ANALYSIS OF RUSSIAN PHOSPHORITE NODULES.

	Per cent.
Phosphate of lime	75·00
Carbonate of lime up to	12·23
Calcium fluoride	6·98
Sulphate of lime	1·60
Phosphate of magnesia up to	1·30
Oxides of iron and alumina	5·00
Organic matter	1·00

The richest and most extensive phosphate deposits are those of Central Russia. They occur chiefly in the governments of Podolsk, Kostroma, Smolensk, Koursk, Woronesch, Simbirsk, Tambow, and on the banks of the Volga, from which they trend towards the West as far as Niemen; they occupy a surface of 20,000,000 hectares (50,000,000 acres). The richest deposits consist in part of phosphate of lime, mixed with organic matter. According to a recent announcement it has been found that the building-stone used in the whole district is nothing but phosphate of lime. That is a highly interesting fact. The phosphorite contains:—

TABLE XXI.—ANALYSIS OF CENTRAL RUSSIA PHOSPHORITE.

	Per cent.
Water	5·10
Phosphoric acid	27·45
Lime	43·00
Carbonic acid	4·60
Oxide of iron	3·40
Oxide of alumina	1·09
Sulphuric acid	1·04
Fluorine	0·47
Silica	13·82

These immense deposits are not utilized. They are to all appearance destined to form the reserve from which Europe will draw when the deposits now being utilized will be exhausted.

VIII. SPAIN.—There exist in the province of Estremadura extensive phosphate deposits, forming well-defined veins. At Logrosan the veins occupy a space of 12 to 20 square miles traversing the granite and the Silurian schists and contain only phosphate and quartz. The phosphate is apatite. It occurs as regular, generally dull hexagonal prisms of a yellowish or greenish colour, and unequal. It is found in its gangue first as more or less voluminous, crystalline fragments of 0·2 to 1 inch in length, then as crystals almost invisible to the naked eye, and distributed

TABLE XXI. (A).—ANALYSES OF SAMPLES OF ESTRAMADURA PHOSPHATES.

	Apatite extracted from Granite.		Phosphorite extracted from Granite.	Phosphorite Fibrous Earthy.		Phosphorite Scaly extracted from Limestone.	Phosphorite Earthy extracted from Limestone.
	Crystallized.	Crystalline.		Extracted from Schist.	Extracted from Limestone.		
Water	—	—	0·25	0·15	0·05	0·85	0·90
Tricalcic phosphate	93·82	89·68	78·16	87·21	74·40	80·77	79·46
Calcium fluoride	5·44	5·38	2·18	8·00	3·08	1·03	4·53
Calcium chloride	0·31	—	0·16	—	—	traces	0·05
Carbonate of lime	—	—	11·30	1·16	20·45	17·00	13·64
Sulphate of lime	—	—	0·92	traces	traces	traces	traces
Silicic acid	0·30	1·90	5·60	2·00	1·10	0·10	0·20
Oxide of iron	—	1·15	1·10	0·84	0·50	0·08	0·90
Oxide of alumina	—	1·30	traces	traces	—	—	—
Manganese dioxide	—	0·39	traces	traces	traces	—	traces
Undetermined	0·13	0·15	0·34	0·64	0·42	0·17	0·33

through the magma of the rock. The Caceres deposits are more extensive, but the material is less rich in phosphoric acid. The veins traverse a compact limestone regarded as Devonian, and disperse themselves in the subjacent schists with thinning-out zones in contact. Phosphate veins also occur in Silurian schists which extend to the north of Alcantara, province of Caceres, of Badajoz, Elvas, Zarza Mayor, Albala, Montanchez, Majadas, Malpartida, Ceclavin, as far as Portalegre and Morvao in Portugal. The size of the veins varies from 20 cm. (8 inches) to 8 metres (25 feet). The phosphate and the containing rock are of the same nature as at Logrosan. The composition of Estremadura phosphate varies very considerably, as the very complete analyses of Schucht reproduced on previous page show. (See also p. 52.)

IX. North America.—There are four centres of phosphate production in North America, viz. Canada, South Carolina, Florida, Tennessee. In addition to these, deposits of less importance occur in North Carolina, Pennsylvania, Massachusetts, Indiana, Kentucky, and Alabama.

Canada.—Deposits of apatite, crystallized in pockets and in veins, are wrought in Canada. The pockets of apatite are met with in beds of pyroxenite of variable magnitude but of great regularity in stratified conformable layers in the gneiss. The paleozoic limestones on which this gneiss lies are of the Laurentian age. The gneiss is itself pierced by numerous crystals of apatite. Apatite is found in the province of Quebec, at Templeton, Buckingham, Portland, Egonville, Lievre-river; in the province of Ontario, at Leeds, Lamarck, Fontenac, Addington, Kingston, Perth, and Renfrew County. The most important deposits are those of North Burgess, South Burgess, and North Emsley in Lawrence County.

The following are three analyses of Canadian apatite by Dr. Voelcker:—

	I.	II.	III.
Moisture, water of combination and loss on ignition	0·62	0·10	0·11
Phosphoric acid[1]	33·52	41·54	37·68
Lime[2]	46·14	54·74	51·04
Oxides of iron and alumina, fluorine	7·82	3·03	6·88
Silica	11·90	0·59	4·29
	100·00	100·00	100·00
[1] Equivalent to tribasic phosphate of lime	73·15	90·68	82·26
[2] Excess lime over the amount required to form tribasic phosphate	6·50	5·60	6·47

The utilization of Canadian phosphates is embarrassed not only by the depression more or less transitory in the price of the material, but further and still more by the irregular mode of occurrence of the deposit, and the obligation created by the dearness of freights and the tariffs imposed in foreign countries of only regarding as marketable and fit for export products containing 80 per cent of tribasic phosphate. Now this content cannot be secured except at great expense, and an enormous waste of low quality material which being unutilizable is piled up on the outskirts of the mines. In fact, no mineral with less than 60 per cent is of any value in Canada, as not being capable of paying for the freight. Trials have been made with the washing processes, with the result that certain deliveries have tested 87·83 of tribasic phosphate of lime. That is the highest figure attained in Canada but working has ceased for some years.

South Carolina.—The South Carolina phosphate deposits occur in Miocene strata from the Charleston basin as far as North Carolina, Georgia, and Florida. They are very extensive, and the nodules of phosphorite extracted therefrom are very similar to those which exist in Central Russia and in the London Basin. They were discovered in 1869, i.e. long before the other North American deposits. The Carolina deposits extend along the coast with a breadth of 10 to 45 miles, from the source of the River Wando and from the eastern arm of the River Cooper, which both flow into the Atlantic at Charleston as far as the sources of Broad River. They are often found on the surface of the ground. At other times they are covered with sand and clay deposited by diluvial water. The rock phosphate is distinguished from the river phosphate (*Land Phosphate* and *River Phosphate*). The first is usually found 10 feet from the surface, the second on or under the beds of the rivers. In colour they vary according to their origin. That of the rock phosphate is yellowish or pale grey. River phosphates are black owing to the presence of organic matter. The phosphorite occurs as nodules or balls, with a rugose surface, and smooth or pitted sometimes shining as if enamelled. It is often mixed with shells, petrified bones, the teeth of terrestrial and marine animals. The diameter of the lumps varies from a few centimetres to 1 metre. Before the discovery of the Florida phosphates, the South Carolina deposits furnished about one-fifth of the world's consumption. The product was perfectly suitable for making superphosphates with 13 per cent of phosphoric acid = 28·4 per cent soluble phosphate. The annual export amounted to 150,000 tons. But since 1890, Florida has continued to increase its production, and the low price caused thereby has led a certain number of those engaged in the industry in Carolina to shut down. Since that time the Carolina production has continually diminished. The average

composition of South Carolina nodules is the following according to Dr. C. W. Shepard of Charleston:—

TABLE XXII.—AVERAGE COMPOSITION OF CAROLINA PHOSPHATE.

	Per cent.
Phosphoric acid	25 to 28
Carbonic acid	5 ,, 11
Sulphuric acid	0·5 ,, 2
Lime	35 ,, 42
Magnesia	traces to 2
Ferric oxide	1 to 4
Fluorine	1 ,, 2
Sand and silica	4 ,, 12
Organic matter and combined water	2 ,, 6
Moisture	0·5 ,, 4

The output of South Carolina increased from 12,262 tons of phosphate rock in 1868 to 618,569 tons in 1893, and then steadily contracted to 169,156 tons in 1911. Most of it is converted into superphosphate locally since the high cost of production inhibits export.[1]

Florida.—This peninsula of the American continent contains, throughout its whole length, phosphatic deposits of great magnitude, which were not utilized prior to the year 1890. Dr. Simmons of Hawthorn in 1879 discovered that the chief quarries of building-stone of Central Florida contained a considerable amount of phosphoric acid. Again, Francis Le Baron, a French engineer of Jacksonville (Fla.), discovered in 1884 the deposits of fossil bones forming the bars of Peace River, and also sent at the time several barrels to the Smithsonian Institution in Washington. This engineer returned to the district in 1886, made measurements and estimated the profits to be drawn from the working of these superficial deposits. When these were published, Col. T. S. Menchald installed in 1887 phosphate works to exploit the nodules, and sent his first delivery to the Scott Manufacturing Co. of Atlanta, Georgia. In June, 1889, Albert Vogt discovered the hard rock phosphate in sinking for water about twenty miles S.W. of Ocala, a small town in Central Florida. The Dunellon Phosphate Co. was then formed to buy and exploit several thousand acres on the alignment of the hard rock phosphate. Since that time the different kinds of phosphate as rocks, and as nodules, have been actively prospected for, and recognized over a tract 200 miles long by 6 miles in width. This belt is developed, parallel with the coast of Florida, at an average distance of 26 miles, and extends from the district of Richland, Pasco County, to the north as far as the environs of the River Apalachicola, bending towards the west and

[1] W. H. Waggaman, Bull. U.S. Dept. Agric. No. 18, 1913.

the south. The most important deposit of nodules (Land Pebbles) was discovered in 1890, in the neighbourhood of Bartow (Palk County). As far back as 1892, both rock phosphates and nodule phosphates were known of varying composition and values far beyond the rivers Apalachicola in the west and north; and Caloosabatchee in the south. Throughout all these districts, representing a length of 400 miles, the exploitation has been followed up with feverish enterprise, and the quantities marketed, not only in the United States but in Europe, have rapidly increased.

Description of the Deposits.—Four kinds of phosphates are differentiated by the following names, viz. Hard Rock, Soft Phosphate, Land Pebbles, River Pebbles.

Hard Rock.—Rock phosphate as a type is hard, compact, with a fine homogeneous grain, usually pale yellow with irregular cavities, often coated with mammillary concretions of phosphate of lime. These cavities are sometimes filled with amorphous phosphate of argillaceous aspect, due to the transport by water of particles of phosphate in suspension. The hard rock deposits of the Eocene are concentrated in a narrow belt about 144 miles long, almost parallel with the West Coast of Florida, and at a distance from the sea varying between 25 to 50 miles. Taken as a whole hard rock occurs as a conglomerate of boulders, cemented by a gangue, consisting of phosphatic sand, clay, or other detritus from the disintegration of the hard rock, and which constitutes the soft phosphate. The magnitude of these deposits of hard rock vary considerably. Near Dunellon they are often 40 to 50 feet thick, elsewhere only 5 to 10 feet. On certain points phosphate is found on the outcrops, especially in Levy County, but more often it is covered by a layer of sand 10 feet thick. There are two kinds of rock phosphate, solid rock and laminated rock. The solid rock is more or less homogeneous, of a white, grey, or yellow colour, sometimes deep blue or black, but more often it is marbled. The hard rock of good quality contains 77 to 82 per cent of phosphate of lime, and 3 per cent of oxides of iron and alumina. An analysis of a fine sample of hard rock gave the following figures:—

TABLE XXIII.—ANALYSIS OF A FINE SAMPLE OF HARD ROCK PHOSPHATE.

	Per cent.
Water	0·92
Calcium fluoride	4·4
Phosphate of lime	83·14
Carbonate of lime	3·63
Oxide of alumina	1·52
Oxide of iron	2·26
Silica	4·13
	100·00

The analyses of two cargoes of 800 tons each, from the Blue River Phosphate Co., gave :—

TABLE XXIV.—ANALYSES OF HARD ROCK BLUE RIVER PHOSPHATE.

	I.	II.
	Per cent.	*Per cent.*
Water	0·52	2·80
Phosphate of lime	81·59	78·19
Oxides of iron and alumina	2·06	2·95

The laminated rock, the crevices of which are generally filled with clay, rarely sand, frequently contain 5 to 8 per cent of clay, from which it is partially freed by roasting, grinding, and sifting. It then contains not more than 3 or 4 per cent of oxides of iron and alumina. The material passing through the sieve contains as much as 10 per cent of clay, and is utilized in the country itself. This roasting of the phosphate is carried out in a very primitive manner: on a layer of wood 1 foot thick is placed a layer of phosphate 3 to 4 feet thick, and fire applied. This method, although economical, yields a bad product. Whilst the phosphate of the lower layer is sufficiently roasted, that on the top is barely dried, and the whole becomes mixed with ashes and pieces of charcoal. But the roasting has little effect on the moisture content of the phosphate: mere exposure to the open air allows it to regain 1 to 3 per cent.

Plate Rock or Sheet Rock.—This kind of phosphate is the most interesting of all. It is found near Ocala, especially near Anthony, Spar, and Montagne. It occurs as small tablets, as large as the hand, of irregular shape, one to several centimetres thick, of a white or brownish-yellow colour. The heavy, brittle fragments are the richest in phosphoric acid, whilst the soft light fragments contain the most clay. The sorted pieces contain sometimes as much as 80 per cent of phosphate, and only 1 to 2 per cent of oxide of iron and alumina; the average being 74 to 78 per cent of phosphate of lime, with 3 to 4 per cent of oxide of iron and alumina. This high iron and alumina content is derived from the gravel mixed with it, which forms irregular fragments of phosphate, the crevices of which are filled with clay. The plate rock rests always on the dolomitic limestone, which forms columns and irregular cones. The cavities contained between these columns are filled with phosphate, mixed with sand or clay. In certain places the phosphate bed is very pure, containing 50 to 80 per cent of pure phosphate. The superficial layer of sand is usually of moderate thickness but it sometimes reaches a depth of 45 to 50 feet.

Soft Phosphate.—There is known under this name, in Florida, a phosphatic clay of soft, friable, or plastic consistency, with a very

variable moisture content, which constitutes the gangue between the pebbles. As the following analyses show, a small portion of its phosphoric acid is soluble in water and in citrate solution :—

Soft Phosphate of Palk County.—Water 8·35 per cent; phosphoric acid, total 28·9 per cent, of which 0·87 per cent is soluble in citrate (Wagner's method) and 2·05 soluble in citrate (Petermann's method) ; 2·83 per cent of oxide of iron, and 0·86 per cent of clay.

Soft Phosphate of Alafia Creek.—Water 5·8 per cent; phosphoric acid, total 9·4 per cent, of which 0·62 per cent is soluble in water ; oxide of iron 7·5 per cent; clay 10·26 per cent. This quality of phosphate is used directly as manure, after being finely ground.

River Pebbles are found in several rivers of the west part of Florida, chiefly in Peace River and Alabama River, where they sometimes form considerable deposits. This phosphate can be extracted more cheaply than any of the others. Powerful dredgers fitted with centrifugal pumps lift the sand and pebbles ; these are afterwards separated from the sand by a slightly inclined rotary sieve consisting of iron rods. The sand passes through the meshes, and returns with the water into the river, whilst the phosphate issues from the sieve at the lower extremity, mixed with stones and pieces of wood. It is taken to the dryer without further cleaning. The daily yield of a dredger varies according to the quality of the material lifted by the pump. Thus on certain points of the river the phosphate is very pure, whilst on others nothing but sand is found. Some days 100 tons of phosphate are collected, other days only 20 tons. The installations at work on Peace River produce on an average 50 tons of phosphate per day. The cost of extraction of river pebbles is in general not heavy, but the cost price per ton exceeds a dollar on an average. The waters of Peace River incessantly bring phosphates to certain points, and remove it from others. Whatever may be the importance of the deposits of Peace River phosphates, they are not inexhaustible, and the time is not far distant when they will cease to be workable. River pebbles are in the form of nodules, the size of which varies from sand grains to nuts. The corners are rounded, and the surface is often polished and brilliant. The colour is dark-grey, blue, or black. The land pebbles, from which the river pebbles are formed by the scouring action of the water, are generally pale, and it is believed that the black colour of the river pebbles comes from the tannin of the plants which grow on the banks of the rivers. Analysis reveals no difference between the two phosphates. Both have the same composition, 65 to 70 per cent of phosphate of lime, with less than 3 per cent of oxide of iron and alumina. The impurities found mixed with river pebbles have, however, the effect of reducing the phosphate of lime to between 60 to 65 per cent.

Land Pebbles.—All the country between Peace River and Alafia River, in the counties of Polk, Hilsborough, de Soto and Manatee, contain phosphate deposits. The richest region is a strip of land about 160 square miles, between Barlow, Fort Meade, Chicora, and Callsville. The land of this district is flat like all South Florida, with low undulations here and there. Under the surface bed of sand, phosphatic clay is found almost everywhere. As already mentioned, land pebbles are not very different to river pebbles. They are paler and purer than the latter; and the phosphate of lime content may reach 72 to 75 per cent, with an average of 66 to 68 per cent, with 2·3 per cent of oxide of iron and alumina. A typical sample gave the following results:—

TABLE XXV.—ANALYSIS OF LAND PEBBLE PHOSPHATE.

	Per cent.
Phosphoric acid	33·61
Loss on ignition	0·79
Lime	48·08
Oxide of iron	1·20
Oxide of alumina	1·38
Magnesia	5·54
Carbonic acid	2·29
Silica	7·15

Tennessee.—As early as 1892, the presence of a very extensive phosphate level in the south of the central region of Tennessee, chiefly in Mount Pleasant County, in the districts of Maury and Perry, was discovered. The bed is found below the Devonian schists of Chattanooga. The phosphate occurs in two distinct forms; in the upper part, that is to say, immediately below the greyish-blue shales of Harpeth, phosphatic nodules are found, then comes a bed of black schists termed Chattanooga, and finally a uniform bed of about 1 metre in thickness of rock phosphate resting directly on limestone, which ends the formation. Samples of this rock phosphate from the best-known localities gave the following average results (D. Levatt):—

TABLE XXVI.—ANALYSIS OF TENNESSEE ROCK PHOSPHATE.

	Per cent.
Phosphoric acid	26·74 to 31·94
Oxide of iron	2·32 „ 6·92
Insoluble matter	2·70 „ 7·06
Lime	29·60 „ 41·30
Sulphur	0·00 „ 4·00
Carbonic acid, (CO_2)	0·00 „ 1·50
Moisture	0·20 „ 0·60

Remarks on the Actual Condition of the Phosphate Industry in America.—In the Southern States of the Union, there is a manifest

tendency to concentrate businesses into the same hands. Thus for the hard rocks of Florida, there were 70 declarations of exploitation in 1902, 60 in 1903, 18 in 1904, 14 in 1905, and 16 in 1906. On the exploitations declared in 1906, 10 were at work, 3 idle, and 3 in preparation. The total amount of rock phosphate marketed in 1906 was 2,080,957 long tons, the value being 8,597,437 dollars, against 1,947,190 long tons in 1905. The production of Florida alone reached 62·4 per cent of the total production of the United States. The exports of hard rock were 565,953 long tons in 1906, against 595,491 long tons in 1905; these figures, however, exceed those of previous years. The exports of land pebbles to America and foreign ports reached 482,232 long tons, against 385,915 in 1905. River pebbles were not exported in the two last years. The South Carolina output has continually decreased since 1893. The production of Tennessee rose in 1906 to 528,888 long tons. Tennessee phosphate occurs in three varieties, which are the blue or black rock, the brown, and the white. The quantities marketed in 1906 consisted of 93 per cent brown, 6·5 blue, and 0·3 per cent white. In the west part of Putnam County, a new deposit of blue rock phosphate has been discovered. This contained on on an average 65 to 75 per cent of tricalcic phosphate and only 5 per cent of oxides of iron and alumina. Amongst the other phosphate producing states, during the years 1901 to 1906, may be mentioned North Carolina, Pennsylvania, Arkansas, and Idaho. But the production of these states was very low, except Idaho. North Carolina produced 45 long tons in 1903, Pennsylvania 100 long tons in 1904. In Arkansas the production continually increases, though slowly. Idaho promises to become a big producer of phosphates. The bed, at a certain place, has a thickness of 85 feet; the main bed is 5 to 6 feet thick.

X. Africa.—*Tunis and Algeria.*—These two countries contain enormous deposits of phosphates. As far back as 1873, Thomas discovered the existence in the region south of the Tell, in the province of Algeria, of a Suessonian formation, rich in phosphate of lime, In 1886, the same geologist, after a scientific expedition, published his first researches on the phosphate beds of the Regency. He had, more especially, examined the deposits in the neighbourhood of Gafsa, in Tunis, showing their continuation through the South Algerian region. The phosphate of these regions is found at the base of the *Eocene* in contact with the *Cretaceous*, from which it is separated unconformably by black muddy clays of variable thickness saturated with chloride of sodium and gypsum, with the characters of silica. These phosphate beds consist of alternations of marl and nodules of phosphatic limestones, covered in the south of the Regency by a bed of shelly limestone, which gives place to a thick formation of nummulitic limestone as it ascends to the

north. The phosphate beds become at the same time more sandy and glauconitic.

Marly Phosphate in Nodules.—The phosphate of lime occurs in nodules; in the foliated and generally highly gypsiferous marls which alternate with limestone beds. Teeth and debris of saurians and fish are found therein. These marls are unctuous and greasy to the touch, and contain as much as 7 to 8 per cent of organic matter the composition of which has not been closely examined, but which does not dissolve in carbon disulphide or in benzine. These foliated marls often pass to a nodular structure. They contain irregular layers of phosphatic nodules which occur in various sizes and shapes, generally rounded or striated, covered with a shining brown crust of characteristic appearance. The large nodules which are met with in these conditions, and which have the appearance of enormous coprolites, are on the contrary very poor. The phosphate is entirely concentrated in the shining surface crust, the internal portion being limestone. The small nodules of identical appearance, on the other hand, may contain as much as 70 per cent of phosphate. The phosphatic marls contain besides phosphates, small interstratified crystals of gypsum, nodules of celestine, strontium sulphate, and alkaline salts.

Phosphatic Limestones.—These phosphates alternate with the nodular marl. They occur in the form of a granular, rather friable rock, the colour of which varies from a yellowish-grey to a greenish-brown. The quality most appreciated may be crushed easily between the fingers, and its density does not exceed 2 for the rock *in situ*. This rock is formed by the agglomeration in a more or less calcareous cement of many fine grains of all shapes; some round, covered with a brown, brilliant crust, consist essentially of yellowish phosphate of lime, with an earthy fracture, or of fibrous appearance; the others, grass green, of scaly texture or in very small masses, of a scoriaceous or corroded appearance, recall, by their appearance, certain glauconites. There also occur very small grains of hyaline angular quartz, and chemical analysis always shows in this rock an appreciable amount of free or hydrated gelatinous silica; finally, it is also very rich in organic debris, such as coprolites, similar to those of the foliated marls, fish or saurian teeth and bones, more or less disintegrated. When the calcareous element predominates in this rock, it becomes greyish, and then much resembles the grey chalk (calcareous tufa) of Ciply. These bands of phosphatic limestone are extensive, occupying a very variable position in the different deposits, although a constant feature of each of them. Their thickness varies from only a few centimetres up to three metres and more, which they maintain without interruption over distances of 50 to 60 km. (western chain of Gafsa). The deposits may be divided into four main groups. 1. Those of the Tebessa

district; 2. Those of the district of Setif; 3 Those of the Guelma district; 4. Those of the Ain-Bejda district. They contain 24 to 30·5 per cent of phosphoric acid.

TABLE XXVII.—COMPLETE ANALYSIS OF AN ALGERIAN PHOSPHATE.

	Per cent.
Moisture	5·03
Loss on ignition (7·5 per cent CO_2)	9·26
Phosphoric acid	30·38
Calcium oxide	49·53
Sulphuric acid	2·01
Oxide of iron	0·32
Oxide of alumina	0·47
Magnesia	1·01
Potash	0·15
Insoluble, etc.	1·85
	100·01

TABLE XXVIII.—ANALYSES OF TWO SAMPLES OF DJEBEL GOURNIA PHOSPHATE IN THE NATURAL CONDITION.

	I. Per cent.	II. Per cent.
Moisture	6·64	8·18
Organic matter	1·24	0·52
Silica	6·80	5·96
Phosphoric acid [1]	24·93	27·01
Carbonic Acid [2]	8·52	7·30
Lime	46·12	45·40
Magnesia	0·11	0·08
Manganese	traces	traces
Fluorine	4·0	4·10
Calcium chloride	8·22	8·43
Oxide of iron	0·98	0·86
Alumina	0·20	0·16
[1] Equal to tribasic phosphate of lime	54·42	58·96
Phosphate of lime on the dry sample	58·30	64·05
[2] Equal to carbonate of lime	19·34	16·57

Egypt.—Several extensive deposits of phosphates have been discovered in Egypt and are now being worked. One of these areas is near the Red Sea, from whence the rock is conveyed by a 20 mile railway to the coast at Port Safaga, at which place the rock is loaded for shipment abroad. The phosphate contains 65 per cent and upwards of phosphate of lime. Other deposits are found at Kosseir and at Sebaia on the eastern bank of the Nile between Keneh and Assouan, and extensive concessions have been obtained by an Italian company for working these deposits. A light railway was under construction in 1914 for connecting the

deposits near Kosseir with the latter place, while at Sebaia the rock is to be conveyed down to the Nile by means of an elevated ropeway, to boats for conveyance to Alexandria for shipment.

According to the Government Survey Department the total output of phosphates in Egypt was as follows: 1908, 700 tons; 1909, 1000 tons; 1910, 2397 tons; 1911, 11,925 tons; 1912, 69,058 tons; 1913 (estimated), about 103,000 tons, almost all of which came from the Red Sea area and practically all of it was shipped to Japan. No superphosphate is at present made in Egypt owing to the difficulty of getting the acid required, but there is a good demand for it, the imports being about 13,000 tons. The manufacture of superphosphates locally has, however, been under consideration, using pyrites from Greece. There has been a reported discovery of pyrites in the Sinai peninsula which may also be available.[1]

XI. Asia.—It has also been found in Palestine, to the west of the Jordan, near to the route followed by the caravans going from Damascus in Arabia, and testing 80 per cent of phosphate of lime, with 1 per cent of iron and alumina, and 10 per cent of calcium fluoride. These deposits are not yet exploited commercially.

XII. Phosphates of Oceania.—There are found in certain isles and on the American Pacific coast considerable deposits of phosphatic material. Like Peruvian guano, which will be dealt with in the sequel, they are of animal origin, but they differ essentially from Peruvian guano owing to the almost complete absence of nitrogen, which they have lost by decomposition and the influence of climatic conditions, having been carried away by rain and percolating water. All phospho guanos resemble each other in their composition. They consist mainly of phosphate of lime, the content of which varies between 65 and 80 per cent and about 12 per cent of water. They moreover contain from 1 to 13 per cent of carbonate of lime derived from the coral limestone which serves to them as substratum, and about 1 per cent of nitrogen yielded by the organic matters which impart to them a colour varying from yellow to dark brown. Finally, small amounts of oxide of iron and alumina, calcium fluoride, and other substances, the presence of which, as will be described later, interferes with the dissolving of the phosphates.

Phospho Guanos were formerly the most highly esteemed raw material for the manufacture of superphosphates and the most easily preserved. Unfortunately, most of the deposits are partially exhausted, and those which still exist are not now worked, owing to the fall in price and the scarcity of labour. Phospho guanos differ much from each other in their appearance, their form, and their colour. They are met with, most often, in a pulverulent

[1] Cham. of Comm. Jour., Oct., 1914.

state, mixed with lumps, easy to crush between the fingers. They sometimes consist of masses, amalgamated with coral debris, sometimes as crusts, or again in masses as hard as stone. The chief deposits of these phosphates are met with in a great number of small islands in the West Indies and the Pacific Ocean, and also in the Bay of Mejillones on the West Coast of South America. A rapid description indicating their characteristics will now be given.

I. *West India Islands.*—Redonda Isles, Sombrero, Navassa, Aruba, Curaçao, Los Roques, Alta Vela, Rata.

II. *Islands of the Pacific Ocean.*—Baker, Jarvis, Malden, Fanning, Starbuck, Howland, Phœnix, Sidney, Enderbury, Minerva, Aves, Lacépède, Flint, Browse (? Brown), Fluon, Chesterfield, Abrolhos, Mona, Cayman, Clipperton, Nauru, Angaur, and Makatea Isles, etc.

West India Islands.—1. *Redonda Phosphate.*—This phosphate, like that of Alta Vela, does not contain phosphate of lime, but hydrated phosphate of alumina and phosphate of iron. It is thus unfit for making superphosphate. It is yellow in colour, more or less dark with black points. Its composition is as follows :—

TABLE XXIX.—ANALYSES OF REDONDA PHOSPHATE.

Analyst.	*Voelcker.* *Per cent.*	*Tate.* *Per cent.*
Water	24·20	21·50
Phosphoric acid	38·52	38·50
Oxide of iron and alumina	35·33	32·50
Insoluble	1·95	6·50

2. *Sombrero Phosphate.*—Two kinds are to be differentiated: one oolitic in structure and variegated in colour, which contains, besides tribasic phosphate of lime, the phosphates of magnesia, iron and alumina, also silica and alumina; the other has a more homogeneous structure, a white or yellowish colour, is rich in phosphoric acid and containing in addition carbonate and sulphate of lime. This deposit was known in 1814, but it was only in 1858 that it commenced to be worked, and since that time there has been taken from it during many years excellent phosphate of lime, containing 75 to 80 per cent of $Ca_3P_2O_8$, 10 per cent of carbonate of lime, and 2 per cent of oxides of iron and alumina. With regard to the quality of the product since it began to be extracted below the sea-level, Voelcker gives the following analysis :—

TABLE XXX.—ANALYSIS OF SOMBRERO PHOSPHATE. (VOELCKER.)

	Per cent.
Water	2·94
Phosphoric acid	35·52
Lime	47·99
Oxide of iron	3·70
Alumina	7·55
Magnesia	0·58
Sulphuric acid	0·36
Carbonic acid	0·96
Fluorine	0·43

3. *Navassa Phosphate.*—The isle of Navassa is of coral origin, with escarpments in some places, and eroded by the waves in others. Phosphate was worked here as far back as 1856, but it was soon found to be rich in oxides of iron and alumina, and on this account was abandoned. It is mostly granular, or in the form of grains, the size of which varies from that of a pin-head to that of the fist, which are often agglomerated into large masses of almost pure phosphate of lime. The composition according to Bretschneider (I) and Gilbert (II) is given below:—

TABLE XXX (A).—ANALYSES OF NAVASSA PHOSPHATE.

	I. Per cent.	II. Per cent.
Water	5·73	3·01
Combined water and organic matter	4·93	7·17
Phosphoric acid	31·69	33·28
Lime	38·00	40·19
Oxide of iron	4·25	11·67
Alumina	8·81	
Sulphuric acid and fluorine	1·10	—
Carbonic acid	2·40	2·15
Insoluble matter	3·09	2·53

4. *Aruba Phosphate.*—This phosphate occurs as yellowish stones traversed sometimes by dark-coloured veins and spots. It contains about 30 per cent of phosphoric acid, and 6 per cent of oxide of iron and alumina.

5. *Alta Vela Phosphate.*—This phosphate has a composition analogous to that of Redonda phosphate, as the following analysis shows:—

TABLE XXXI.—ANALYSIS OF ALTA VELA PHOSPHATE.

	Per cent.
Phosphoric acid	37·00
Oxide of iron	24·00
Alumina	15·00
Lime	1·00
Sesquioxide of chromium	0·75

6. *Rata or Fernando Noronjo Phosphate.*—This phosphate occurs as a fine powder; it also is very rich in oxides of iron and alumina, and thus unfit for superphosphate manufacture. It contains about 26 per cent of phosphoric acid and up to 20 per cent of oxides of iron and alumina.

7. *Monk's Island (Caribbean Sea) Phospho Guano.*—This phosphate contains 42 per cent of phosphoric acid and only 40 per cent of lime. It consists therefore partially of monacid phosphate. Its analysis gave the following results:—

TABLE XXXII.—ANALYSIS OF MONK'S ISLAND PHOSPHATE.

	Per cent.
Nitrogenous organic matter and combined water	7·60
Sulphate of lime	8·32
Phosphate of lime and magnesia	70·00
Alkaline salts	1·88
Carbonate of lime / Carbonate of magnesia	10·20
Insoluble silicious residue	2·00
	100·00

The surface of this deposit, which is as hard as a rock, has not the same composition as the interior. Thus the bed having been carefully analysed yielded 70 per cent of phosphate of lime on the surface, 74 per cent in the centre, and 75 per cent in the lower portion.

8. *Christmas Island Phospho Guano* (Indian Ocean).—Christmas Island, to the south of Java, belongs to the Straits Settlements. The phosphate deposit discovered there a few years ago is worked by a British Company, The Christmas Island Phosphate Co. Ltd. The total bulk of this deposit is estimated at 250,000 tons, with a percentage of 60 to 90 of phosphate of lime. The samples received in Europe tested 85 per cent of phosphate of lime with 1·5 per cent of sesquioxides; and after being rendered soluble by sulphuric acid at 53° B., it yielded about 20 per cent of phosphoric acid, of which 0·5 per cent was insoluble in water, and 4 per cent free, which is moderate. This phosphate is very hard, but easy to crush after it has been dried, which is indispensable, since it contains 5 per cent of moisture.

Pacific Ocean Isles.—There are a series of small coral isles in the Pacific Ocean, in the neighbourhood of the equator, destitute of all vegetation, which have attracted but little attention. A sample was brought in 1853 to America of a non-nitrogenous guano, collected in one of these islands—Baker Island. Soon afterwards it was found that the other isles of the same group were equally rich in guano,

viz. Howland, Malden, Jarvis, Starbuck, Enderbury, and finally the Phœnix Isles, a little further west. As Baker Isle, now for the most part exhausted, yielded the best guano, the typical guano of the isles of the group, a short description of it is now given.

Baker Island Guano.—Baker island is situated at 0·14 of north latitude and 176·22½ degrees of longitude west of Greenwich; 1750 metres (say 1 mile) long, its width is 1100 metres, and its height above the level of the sea is about 8 metres (26 feet). The chain of coral rocks which surround it is dry over a surface of 160 metres. On this chain is a height of stones, corals, and shells which surround the actual guano deposit.[1] The vegetation of the island only comprises rare species. The bed of guano is 15 cm. (6 in.) thick on the shore, and 1·60 metres, say 5½ feet, in the centre. Its surface is plane, and it occupies a surface of 62·5 hectares, say 156¼ acres. The coral isles are the refuge of sea fowl, which come there to make their nests and hatch their eggs. Their excrements, the food which they bring there (fish and other marine animals), and finally their dead bodies, give rise to the formation of guano, which is, therefore, constantly in course of formation. Judging from its method of formation, this guano, like that of Peru, to be described later, should be very rich in nitrogen, but this is not the case. Although rain is generally a rare phenomenon in these tracts, yet the guano is constantly washed by the waves, which are continually broken against the coral chain which fringes the islands. To this has to be added the heat of the day, which is very intense. Owing to the intense bacterial action the nitrogenous matters are rapidly decomposed, producing ammonia and nitric acid; the first is carried away by the wind, the second is converted into nitrate of soda, which is lost in solution in the water of the ocean. All the Pacific guanos are met with as a fine pale or dark brown powder according to their percentage of moisture. The brown powder is mixed with larger white granules, consisting for the most part of phosphate of ammonia and magnesia.[2] According to an analysis of Liebig, Baker Island guano contains:—

[1] The Pacific Isles are all protected on the sides of the prevailing winds by a chain of coral against which the waves of the sea break.

[2] It follows from later researches, that the magnesium phosphate in the guano is not tribasic but monacid; only traces of carbonate of lime were found therein. The composition of the guano is slightly modified since it has been worked in an intensive manner. A few per cents of carbonate of lime are always found in it, and only 75 per cent of tribasic phosphate of lime. The above analysis is typical of this class of guanos when they do not contain large amounts of gypsum, sand, and analogous impurities as do certain guanos from Jarvis Island.

TABLE XXXIII.—ANALYSIS OF BAKER ISLAND GUANO.

	Per cent.
Tribasic phosphate of lime	78·79
Tribasic phosphate of magnesia	6·12
Iron phosphate	0·12
Sulphate of lime	0·13
Alkalies	0·85
Chlorine	0·13
Ammonia	0·07
Nitric acid	0·45
Water, sand, etc.	13·34
	100·00

Baker island was the first island in the Pacific Ocean in which guano was discovered and exploited. The deposit is now partially exhausted.

Other isles in the Pacific Ocean contain vast quantities of phospho guano, similar in composition to that of Baker Island. But the greater part of these deposits are only of historical value seeing that, if they are not exhausted, their output is but small. Thus taken altogether the deposits of Baker Island, Lacépède, Malton, and Pelsart, would appear to be far from exhausted; they probably still contain enormous quantities of guano. But the greater number of the islands have been abandoned, because the cost of working and freights are too high compared with the selling price of the guano, which latter cannot at the present time compete with mineral phosphate.

Jarvis Guano is a mixture of powder, hard plates, and somewhat friable stratified fragments. The plates have a procelain-like character sometimes semi-transparent and have already been found in analogous guanos. Perfectly dried in an oven at 100° C. (212° F.) these fragments preserve their appearance. By detaching the stalagmites, which cover the plates, it has been found that the latter owe their semi-transparent appearance to the hydration of the phosphate of lime, which has evidently been precipitated very slowly. The phosphate so hydrated cannot, in fact, lose its water, except at a red heat, and the hard Jarvis plates dried at 100° C. still contain 11 or 12 per cent, which analysts have often confounded with organic matter, since it is lost when the manure is ignited after simple drying in the oven. This physical state of the phosphate of lime may be understood by considering the phenomena which have successively led to the evaporation of the nitrogenous substances in the guano. Such phenomena cause the partial solution of the phosphate of lime, then later on, its slow precipitation by the ammonia liberated, hence the explanation of the stalagmites and the hydration so conducive to the solubility of the manure in the soil.

TABLE XXXIV.—ANALYSIS OF JARVIS GUANO.

		Per cent.
Phosphate of lime	$3CaO,P_2O_5$ = 17·397 ; $2CaO,P_2O_5$ = 16 026	33·423
Phosphate of magnesia		1·241
Phosphate of iron		0·160
Sulphate of lime		44·549
Sulphuric acid, potash, chlorine; Organic matter and water		20·880
		100·253

The following are some analyses of phospho guanos by Dr. H. Gilbert :—

TABLE XXXV.—ANALYSES OF FANNING ISLAND GUANO.

	Per cent.	or	Per cent.
Water	8·0	Water	8·00
Carbonic acid	1·30	Carbonate of lime	2·97
Sulphuric acid	0·19	Sulphate of lime	0·32
Phosphoric acid	34·16	Tribasic phosphate of lime	73·00
Lime	42·84	Tribasic phosphate of magnesia	1·33
Magnesia	0·61	Calcium fluoride	2·06
Fluorine	1·01	Organic matter	12·32
Organic matter	12·32		100·00
	100·43		
Deduct oxygen equal to the fluorine	0·43		
	100·00		

TABLE XXXVI.—ANALYSES OF BROWN ISLAND GUANO.

	Per cent.	or	Per cent.
Water	15·00	Water	15·00
Carbonic acid	1·48	Carbonate of lime	3·36
Sulphuric acid	1·01	Sulphate of lime	1·72
Phosphoric acid	31·40	Tribasic phosphate of lime	6[illegible]·00
Lime	39·94	Tribasic phosphate of magnesia	0·46
Magnesia	0·21	Oxide of iron	0·32
Oxide of iron	0·32	Sodium chloride	0·14
Soda	0·06	Calcium fluoride	0·70
Chlorine	0·08	Organic matter	10·30
Fluorine	0·34		100·00
Organic matter	10·30		
	100·14		
Deduct oxygen equal to fluorine	0·14		
	100·00		

TABLE XXXVII.—ANALYSES OF LACÉPÈDE ISLAND GUANO.

	Per cent.	or	Per cent.
Water	12·40	Water	12·40
Carbonic acid	0·86	Carbonate of lime	1·95
Sulphuric acid	0·10	Sulphate of lime	0·17
Phosphoric acid	33·64	Tribasic phosphate of lime	71·04
Lime	40·80		
Magnesia	0·93	Tribasic phosphate of magnesia	2·03
Oxide of iron	0·75	Oxide of iron	0·75
Sodium	0·06	Sodium chloride	0·16
Chlorine	0·10	Calcium fluoride	1·58
Fluorine	0·77	Organic matter	9·92
Organic matter	9·92		
	100·33		100·00
Deduct O = F	0·33		
	100·00		

Mejillones Guano.—This guano, so appreciated formerly, is now only of historical interest. From the rocky coast, for a length of almost twenty-five miles, which Bolivia has conquered from Peru and Chili, there emerges a promontory about ten miles long which juts into the sea for a length of three miles, under the tropic of Capricorn, the rocks of which form a protection to the Bay of Morena on the south, and to the Bay of Mejillones on the north. This latter bay, well-sheltered from wind and wave by the point of Leading Bluff Peninsula, forms an excellent harbour, into which the ships come to load guano. The country, moreover, is most unhealthy. The complete absence of rain, the frequency of violent winds and dense fogs which last for many hours, followed by a torrid heat under a brazen sky, a rocky, sandy soil void of all vegetation, and above all, the want of potable water, renders a sojourn in these tracts exceedingly trying. The inhabitants of the capital—the number of which was formerly very small, and has not increased by the working of the guano—are revictualled by the Pacific steamers, which call there and possess coaling-stations. Water is obtained by distilling sea water. The rocky peninsula averaging in height 350 to 400 metres has the appearance of a sandy plain, only its promontory which protects the bay is more elevated, for it rises to 1000 metres (3200 feet) to the west of the town; to the north of this hill is the culminating point of the promontory, called Morro de Mejillones, of a height of 866 metres (2730 ft.). On the slope of this mountain, on the bay side, is the guano deposit. It is reached by a long road from the town, winding round the mountain. The principal deposit is found about 560 metres (1836 feet) above sea-level on the flank of the mountain; in several points it is 14 metres, or 46 feet, thick. The published information on the extent of these

deposits differ considerably; official data place it at 3,000,000 to 4,000,000 tons but other information represent the situation under a less alluring aspect, and assert that the reserves are almost exhausted. A road has been built, with great difficulty, across the mountain to connect the deposit with the loading quay. At a mile from the works the road divides into two—the one at a very rapid incline leads to the harbour, whilst the other leads to an encampment constructed on the edge of the plateau where the guano, which is lifted there in sacks, is run into a shoot 233 metres deep, which delivers it into a warehouse situated in the port. In the centre of the port dwell the workmen, the overseers, the exporters, and the state government employees. The latter weigh the guano, which is then conveyed in trucks on rails to the other extremity of the harbour, and discharged into ships. The formation of Mejillones guano is analogous to that of Baker guano. As the climate here also is very dry, the absence of nitrogen can only be due to the possible contact of sea water. The volcanic nature of these countries being granted, the periodical upheavals and sinkings of the ground are historical facts, and it is known that on these occasions violent high waves are frequent.

Mejillones Guano, like Baker guano, is a brown powder mixed with more or less large friable lumps, consisting in part of phosphate of ammonia and magnesia. In the early days, this guano was frequently mixed with granite chips, from the rocky bed on which the deposits lie. But later the importers installed crushers and driers, which have enabled them to eliminate the stones and to dispatch the guano as a uniform powder. Amongst the numerous analyses published, that by Fresenius and Neubauer is reproduced here. These chemists found in the sample dried at 100° the following results:—

TABLE XXXVIII.—ANALYSIS OF MEJILLONES GUANO.

	Per cent.
Tribasic phosphate of lime	60·564
Monacid phosphate of lime	17·960
Sulphate of lime	1·069
Carbonic acid	2·052
Phosphate of iron, etc.	0·072
Water and organic matter	10·161
Ammonia calculated as oxide	0·018
Sulphate of magnesia	1·528
Nitrate of magnesia	0·034
Common salt	3·739
Total phosphoric acid	38·404
Nitrogen	0·729

Dr. Gilbert gives the following analysis :—

TABLE XXXIX.—ANALYSIS OF MEJILLONES GUANO.

	Per cent.
Water	9·14
Carbonate of lime	0·32
Sulphate of lime	3·26
Phosphate of lime basic	33·64
Phosphate of lime monacid	26·44
Phosphate of magnesia monacid	10·35
Oxide of iron and alumina	1·35
Silica	0·89
Sodium chloride	7·32
Organic matter	7·29
	100·00

As will be seen from these analyses, about one-fourth of the phosphoric acid is combined with magnesia. And if the phosphate of magnesia is in itself more soluble than phosphate of lime, it is so to a still greater extent in the case of monacid phosphate of magnesia.

Clipperton Island Guano.—The discovery of guano deposits in Clipperton Island is more recent. This island is situated in the open sea off the coast of Brazil. The coral chain surrounds a fresh-water lake in mid-ocean and has served as a refuge to sea birds for thousands of years. Whilst the nitrogen of the excrement was carried away by rain water the phosphoric acid combined with the lime of the coral. The whole of the isle is covered with phosphate to a depth of six feet. The average analyses of thirteen samples taken in different sections has given 83 to 86 per cent. of tribasic phosphate and 0·03 of oxide of iron and alumina. In the dry state the phospho guano is a yellowish sandy powder. Dr. Gilbert gives the following analysis :—

TABLE XL.—ANALYSIS OF CLIPPERTON ISLAND GUANO.

	Per cent.
Water	3·80
Tribasic phosphate of lime	78·09
Phosphate of magnesia	0·55
Carbonate of lime	6·73
Quicklime	2·84
Sulphate of lime	0·78
Sodium chloride	0·15
SiO_4	0·28
Organic matter	4·83
Oxide of iron and alumina	0·04
Undetermined	1·91
	100·00

The points of the Chipana Coast, Pabellon de Pira, Punta de Lobos, Huanillos, the Ballestas Isles, Guânape, Macabi, Lobos de Afuera, etc., contain considerable deposits

Nauru Guano.—Nauru Isle, near to the Marshall Isles, is in 0·26 of S. latitude and 166·55° of E. longitude. Whilst the atolls of the Pacific scarcely rise 3 metres (10 feet) above high water, the Isle of Nauru rises about 75 metres, with an area of 2000 hectares (5000 acres). A bank of coral chains 60 to 90 metres wide (195·6 to 295·2 feet) encircles the island. To that succeeds a flat zone 100 metres wide covered with coconut trees; behind rises a rocky region, which consists of a mass of phosphate of great richness. No one knows the depth of this deposit, but the beds are so extensive that their working may last for several generations. The quality of this phosphate would appear to be superior to that of all the phosphates hitherto examined, both as regards the richness and regularity of the phosphoric acid content, 86 to 87 per cent $Ca_3P_2O_8$, as well as the small proportion of oxide of iron and alumina.

A large part of the exports of Nauru phosphate goes to countries washed by the waves of the Pacific, Japan, Australia, New Zealand, and Honolulu, but France, Belgium, Great Britain, Sweden, Norway, Russia, and especially Germany, likewise import large quantities.

Angaur Island Phosphate.—The deposits of Angaur Island phosphate comprise about 2,500,000 tons which may be extracted in the open air. Four-fifths of the deposit consist of a phosphate with a content of 80 per cent of tribasic phosphate of lime. The working was originally leased for thirty-five years to a German company with a capital of 4,500,000 marks, say £225,000.

Makatea Isle Phosphatic Deposits.—There has been discovered in the island of Makatea deposits of phosphate containing, according to the analyses made, from 60 to 85 per cent and even 90 per cent of pure phosphate of lime. Makatea Island belongs to the Paumotou Archipelago, and lies 120 miles to the north of Tahiti. It is 4½ miles long and 1½ miles wide. Its formation differs from all the other islands of the Paumotou group, in that it has no lagoon, and rises up to 230 feet, whilst the other islands are simple chains of an average height of 8 feet above sea-level. Phosphate has been found in several of these atolls, especially in that of Niau. Guano has also been found in Puka-Puka in the extreme north-west of the group.

The deposits of Makatea are estimated at 30,000,000 tons and will be exploited by a French company.

Imports of Guano, etc., taken from the Annual Reports of the Chief Inspector of Alkali Works:—

Tons.	1908.	1909.	1910.	1911.	1912.	1913.	1914.	1915.
Guano	34,417	20,321	7,000	34,124	14,115	25,548	39,285	26,720
Mineral phosphate	530,177	451,807	455,500	493,413	520,270	539,016	555,605	374,639
Sodium nitrate	145,724	90,207	120,600	128,487	123,580	140,926	171,910	132,158

Distribution of Phosphates in the Different Geological Formations.—On examining the subject from a geological point of view, phosphoric acid, or phosphoric acid and nitrogen, is found in the following formations:—

I. *Gneiss Epoch*, as apatite in Sweden, in Finland, in Norway, in the mountains of the east coast of North and South America.

II. *Palæozoic (or Primary) Epoch.*—1. *Silurian Formation.*—As phosphorites in Spain and in the South of Russia. 2. *Devonian Formation.*—As phosphorites in Germany. 3. *Carboniferous Formation.*—As Blackband in Great Britain and Germany.

III. *Mesozoic or Secondary Epoch.*—1. *Trias Formation.*—As Bone Bed and fossil bones in England, Germany, and Switzerland. 2. *Jurassic Formation.*—As coprolites in Germany and England. (*Lias.*)—As phosphatic nodules in France and Germany. (*Osteolithes.*)—As phosphorite in French Jurassic marls. 3. *Cretaceous Formation.*—As coprolites in France, in England, in Germany, and in Holland. As phosphorite in Spain, in Belgium, in France, in Austria-Hungary, and in Russia.

Cainozoic or Tertiary Epoch.—*Eocene Formation.*—As coprolites in England and Germany. As phosphates in France, Algeria, Tunis, the Carolinas, Tennessee and Florida.

Quaternary and Recent Epoch.—1. As *fossil bones.*

2. As phosphate in the islands of Navassa, Redonda, Rata, St. Martin, Curaçao, Testigos, Buenos Aires.

3. As guano crusts in the islands of Starbuck, Flint, Sombrero, Avalo, Los Roques. As phospho guano in the islands of Baker, Howland, Fanning, Jarvis, Malden, Mary, Enderbury, Phœnix, Sydney, Vivorilla, Mona, George, Raza, Clipperton, Monk's at Mejillones, in the islands of Leysan, French, Frigatte Shoal, at Bramble Cays, Shoal Bay, Shark's Bay, in the islands of Timor, Ashmore, Brown, Jones, Lacépède, Abrolhos, Huon, Birds, Kurian, Murian, Swan, and at Algoa Bay.

4. As guano in Peru, Chili, Patagonia. In the islands of Galapagos, Bat, Ichaboe, Damaraland, and Saldanha Bay.

5. Bat guano on the Mediterranean coasts, Egypt, Sardinia, Galicia, Porto Rico.

It will be convenient to add to this classification the substances containing phosphates manufactured by industry, such as bone black (spent char), bone ash, artificial guano manufactured from the excrements and the dead bodies of animals, fishes, and crustaceans; in addition to the precipitated phosphate of the glue and gelatine factories, and finally the phosphates of basic slag. The following table prepared by Dr. M. Ullmann contains the analyses of all phosphates known up to the present time. As this document is absolutely unique in scientific literature it is reproduced here at the risk even of repeating what has been given.

Geographical Distribution of Phosphate of Lime and

Localities.	Longitude of Greenwich.	Latitude.	Designation.	Analysis. Water.	Loss on Ignition.	Lime.
A. Europe.						
1. *Sweden and Norway.*	Degrees.	Degrees.		Per Cent.	Per Cent.	Per Cent.
Krageroe	11 E.	59 N.	Apatite	0·45	—	45·58
Langesund	9·7 E.	59 N.	Chlorapatite . .	0·32	—	51·02
2. *Germany.*						
Hartz	11 E.	52 N.	Apatite	1·2	—	—
Helmstedt	11 E.	52 N.	Phosphorite . .	4·2	—	—
Wasserleben . . .	11 E.	52 N.	,, . .	6	—	—
Lahn et Dill . . .	8 E.	50·5 N.	,, . .	3·85	—	37·31
Peine	10·2 E.	52·3 N.	Coprolites . .	—	—	—
Horde	7·5 E.	51·5 N.	Phosphorite . .	—	—	—
Amberg	12 E.	49·5 N.	Osteolite . . .	—	—	—
Delme (Lorraine) . .	6 E.	49 N.		—	—	—
3. *Austria-Hungary.*						
Schlaggenwald (Bohemia)	13 E.	50 N.	Apatite . . .	—	—	—
Lavanthal (Carinthia) .	15 E.	47 N.	Phosphorite . .	—	—	—
Starkenbach (Bohemia) .	15·5 E.	50·5 N.	Coprolites . .	—	74·03	12·26
Cracow (Galicia) . .	20 E.	50 N.	Bat guano . .	7·50	75·20	—
4. *Belgium.*						
Liége	5·5 E.	50·6 N.	Phosphatic chalk	0·93	2·83	40·64
Ciply	4 E.	50·5 N.	,, ,,	1·52	—	45·45
5. *France.*						
Bellegarde-sur-Rhône .	4·5 E.	43·7 N.	Coprolites . .	4·76	0·2	32·50
Somme	2 E.	50 N.	Phosphorite . .	1·69	—	47·84
Lot	1·5 E.	44·5 N.	,, . .	4·27	—	50·10
Vaucluse	5 E.	44 N.	,, . .	2·45	—	26·57
Ardennes	4·6 E.	50 N.	,, . .	—	—	—
Boulogne	1·5 E.	50·7 N.	Coprolites . .	0·84	3·14	38·06
6. *Italy.*						
Sardinia (Cagliari) . .	9 E.	39 N.	Bat guano . .	18·77	61·14	5·17
7. *Spain.*						
Caceres	6·5 E.	39·5 N.	Phosphate . .	0·721	—	—
Estremadura	6 W.	40 N.	Phosphorite . .	0·30	—	43·41

Guano Deposits and their Chemical Composition.

Analysis.									
Lime not Combined with P_2O_5.	Oxide of Iron.	Alumina.	Magnesia.	Phosphoric Acid.	Nitrogen.	Tribasic Phosphate of Lime.	Carbonate of Lime.	Calcium Fluoride.	Analyst.
Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	
—	1·00	0·77	—	34·30	—	74·87	—	—	A. Retter
—	0·90	—	0·80	38·02	—	82·99	—	—	E. Güssefeld
	2·4		—	18·32	—	35·45	7·10	—	
—	2·86	—	—	19·27	—	41·48	8·9	—	
—	1·72	—	—	18·18	—	39·70	7·9	—	E. Schulte
—	4·75	3·08	0·18	29·19	—	63·72	—	4·88 fluorine	Dietrich & König
—	Very rich in iron		—	34·35	—	abt. 75	—	—	
—	Up to 19 % of iron		—	19·5-21	—	44·20	—	—	
—	—	—	—	36·64	—	80	—	3·0	
—	Phosphate of iron & alumina 13-20 %		—	18·04	—	33·44	—	—	
—	—	—	—	30·59	—	66·79	8·54	5·26	Meusel
—	—	—	-	29·30	—	64·39	13·5	—	
—	—	—	1·31	6·99	—	15·25	—	—	Reuss
—	—	—	-	3·82	9·17	8·33		—	Scheibler
—	2·39		0·79	27·25	—	59·49	7·04	—	Anglo-Cont. G. W.
19·18	1·75	1·11	—	22·17	—	48·44	—	—	A. Grimm
—	16·90	—		12·12	—	26·40	—	—	Dugléré
9·17	2·21		0·78	32·25		70·42	9·10	—	A. Grimm
—	2·96		0·26	37·07	—	80·92	3·43	—	Ulex
—	3·30		0·33	19·90	—	43·44	0·84	—	E. Güssefeld
—	4·6	2·3	—	18·04	—	36·43	10·13	3·0	Delattre
—	2·89	3·09	0·58	21·06	—	45·97	—	—	
—	trace	trace	0·86	5·02	5·72	10·95	—	—	Pavesi & Rotond
—	0·91	0·427	—	29·455	—	59·594	13·227	0·983	
4·85	1·64		—	32·60	—	71·16	—	2·57 fluorine	Niederstedt A. Grimm

Geographical Distribution of Phosphate of Lime and

Localities.	Longitude of Greenwich.	Latitude.	Designation.	Analysis. Water.	Loss on Ignition.	Lime.
	Degrees.	Degrees.		Per Cent.	Per Cent.	Per Cent.
Logrosan	5·5 W.	39·4 N.	Phosphorite	2·40	—	—
Truxillo	6 W.	39·5 N.	,,	—	—	—
8. *Russia.*						
Podolia	27·5 E.	48·5 N.	Phosphorite in balls	—	—	—
Kursk	36 E.	52 N.	Phosphorite	3·57	—	—
Woronesch	39 E.	52 N.	,,	—	—	—
9. *Great Britain.*						
Ipswich (Suffolk)	1 E.	52 N.	Coprolites	—	—	—
Cambridge	0 E.	52 N.	,,	4·01	—	45·39
Bedford	1·5 E.	52 N.	,,	—	—	—
Wales	4 W.	52 N.	,,	1·4	—	23·49
Lyme Regis	3 W.	50·7 N.	,,	6		—
Goodrich	2·5 W.	52 N.	Mineral phosphate	—	—	42·84
B. North America.						
10. *Canada.*						
Ontario	80 W.	4[illegible] N.	Apatite	0·08	—	—
Ottawa	75 W.	45 N.	,,	—	—	—
11. *United States.*						
New York	75·5 W.	44·4 N.	Apatite	0·2	—	51·48
South Carolina	80 W.	33 N.	Phosphate	1·56	—	42·28
Charleston	80 W.	33 N.	,,	9·95	6·65	31·12
Port Royal	81 W.	32·5 N.	,,	0·58	1·01	37·79
Tennessee	86 W.	35 N.	,,	0·80	—	50·60
Florida	80 W.	25·30 N.	,,	0·55	—	50·46
Tallahasee	84·4 W.	30·5 N.	,, (Hard rock)	0·25	—	—
Barlow	82 W.	28 N.	,, (Land pebbles)	—	—	—
Peace River	82 W.	27·5 N.	,, (River pebbles)	1·05	—	—
C. West Indies and Mexico.						
12. *West Indies.*						
Havana	82·5 W.	23 N.	Phosphate	11·90	—	—
Guanahani	74·3 W.	24 N.	Phospho guano	9·83	—	30·60
Vivorilla (Isle)	—	—	,, ,,	7·0	6·46	45·26
Puerto Rico (Ponce)	67 W.	18 N.	Bat guano	17·68	51·66	10·17

Guano Deposits and their Chemical Composition—continued.

Analysis.									
Lime not Combined with P_2O_5.	Oxide of Iron.	Alumina.	Magnesia.	Phosphoric Acid.	Nitrogen.	Tribasic Phosphate of Lime.	Carbonate of Lime.	Calcium Fluoride.	Analyst.
Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	
—	2·22		—	38·95	—	85·03	10·35	—	De Luna
—	little	—	—	35·50	—	75·80	little	14·0	
—	—	—	—	34·0	—	74·23	6·92	—	
—	1·95	—	—	35·42	—	77·34	—	—	Schwackhöfer
—	—	—	—	13·74	—	30·0	24	—	Pieper
—	5·0	4·0	—	24·73	—	54·0	10·0	3 fluorine	Völcker
—	1·87	2·57	0·48	26·75	—	57·12	—	—	,,
—	—	—	—	18·32	—	about 40	—	—	
—	7·47	5·70	—	15·4	—	33·62		—	Herapath
—	1·00	—	—	27·95	—	6·1	24·0	—	
—	2·36		—	27·63	—	60·32	9·54	—	
—	—	—	—	39·98	—	86·61	4·47	7·22	W. R. Hutton
—	0·09	0·57	0·15	39·0	—	85·24	0·06	6·8	
—	1·07		—	37·0	—	79·59	2·32	6·42	H. Gilbert
—	—	—	—	26·89	—	58·70	—	—	Völcker
—	2·86	2·38	1·62	20·92	—	45·66	—	5·11 of fluor.	Ulex
—	2·82	1·12	0·5	23·67	—	51·67	9·18	—	
7·20	3·32		—	36·69	—	80·09	—	—	H. Grimm
9·12	1·95		—	35·80	—	78·15	—	—	,,
—	0·82	1·27	—	35·42	—	77·32	—	—	Pieper
—	0·80	1·37	—	31·59	—	68·96	—	—	Völcker
—	0·52	1·64	—	28·08	—	61·30	—	—	Gilbert
—	2·88	—	—	34·08	—	74·40	—	—	Pieper
16·98	5·77		—	11·60	0·73	25·32	—	—	A. Grimm
—	0·25		1·27	32·24	0·13	70·38	—	—	H. Gilbert
—	1·59		0·17	7·57	8·35	16·52	—	—	A. Grimm

Geographical Distribution of Phosphate of Lime and

Localities.	Longitude of Greenwich.	Latitude.	Designation.	Analysis. Water.	Loss on Ignition.	Lime.
13. *Lesser Antilles.* (*a*) Windward (Isles).	Degrees.	Degrees.		Per Cent.	Per Cent.	Per Cent.
Avalo (Isle)	81 W.	22 N.	Guano in crusts	20·12	—	31·15
Navassa (Isle)	75 W.	18·2 N.	Coralline phosphate	2·7	—	37·6
Mona (Isle)	67·5 W.	18·1 N.	Phospho guano	7·66	—	—
Sombrero (Isle)	63·5 W.	19 N.	Guano in crusts	9·06	—	36·17
St. Martin (Isle)	63 W.	18 N.	Mineral phosphate	5·04	—	47·69
Redonda (Isle)	62 W.	17 N.	Phosphate of alumina	23·23	—	—
Alta Vela	71·5 W.	17·5 N.	,, ,,	16·49	—	—
14. *Lower Antilles.* (*b*) Leeward (Isles).						
Aruba (Isle)	70 W.	12·5 N.	Mineral phosphate	3·46	—	48·72
,, ,,	—	—	,, ,,	2·16	—	47·84
Curaçao (Isle)	69 W.	12 N.	,, ,,	0·84	—	51·00
Buenos Aires (Isle)	68 W.	12 N.	,, ,,	20·0	—	—
Los Aves (Isle)	67 W.	12 N.	Phospho guano	5·93	—	37·92
,, ,, ,,	—	—	,, ,,	10·35	—	—
,, ,, ,,	—	—	,, ,,	14·90	—	—
Los Roques (Isle)	66·5 W.	12 N.	Guano in crusts	10·22	10·22	38·67
,, ,, ,,	—	—	Phosphate of iron	—	—	—
Testigos Isle	63 W.	12 N.	,, ,,	12·17	12·17	0·37
15. *Mexico.*						
George (Isle)	113 W.	31 N.	Phospho guano	—	—	—
Raza (Isle of)	113 W.	29 N.	,, ,,	4·08	—	35·28
Clipperton (Isle)	108 W.	9 N.	,, ,,	3·80	4·83	49·25
D. South America.						
16. *Venezuela.*						
Maracaibo (Monkey Island)	71 W.	12 N.	Phospho guano	2·39	—	39·48
17. *Brazil.*						
Fernando Naronha (Isle of Rats)	33 W.	4 S.	Phosphate	10·0	—	30·6
18. *Patagonia.*						
East Coast	67·5 W.	49 S.	Guano	16·15	28·06	29·20
Falkland (Isle)	60·0 W.	52 S.	,,	8·86	17·10	—

Guano Deposits and their Chemical Composition—continued.

Analysis. Lime not Combined with P_2O_5.	Oxide of Iron.	Alumina.	Magnesia.	Phosphoric Acid.	Nitrogen.	Tribasic Phosphate of Lime.	Carbonate of Lime.	Calcium Fluoride.	Analyst.
Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	
—	5·88	trace	0·44	24·36	0·45	53·18	—	—	A. Schlimper
—	14·8		0·6	33·5	0·11	73·13	5·6	—	Ulbricht
—	0·75		—	27·85	0·25	60·79	3·80	—	Weiss
—	2·42	6·89	0·36	34·41	—	74·55	—	—	Völcker
—	1·21	2·99	0·38	24·14	—	52·70	32·27	—	,,
—	36·38		—	36·95	—	80·66	—	—	,,
11·25	19·24		—	20·45		44·64	—		,,
—	3·25		—	36·29	—	79·22	—	—	E. Güssefeld
—	1·36	0·61	trace	33·82	—	71·65	10·66	—	A. Retter
—	0·2	—	0·97	39·96	—	87·23	6·99	0·48 fluorine	E. Güssefeld
—	—	—	—	21·76	—	45·50	—	—	,,
6·79	1·02		—	26·32	0·36	57·45	—	—	A. Grimm
—	0·164	—	—	29·02	—	63·37	12·83		
—	0·35		—	22·40	—	48·90	7·05	—	
—	0·40	—	2·75	40·49	—	60·80	—	—	Taylor.
—	40·5		—	37·0	—	80·77	1·0	—	Schucht
—	13·30	—	0·57	17·41	—	38·0	—	—	Ure & Teschenmacher
—	1·50	—	—	37·71	—	82·33	—	—	E. Güssefeld
—	1·14	—	1·18	39·70	0·40	86·66	—	—	Fr. Voigt
—	0·04		0·25	36·07	0·06	78·84	6·72	—	H. Gilbert
—	—	—	1·17	41·34	0·139	90·24	—	—	Vöckler
—	9·56	11	—	26·5	—	—	—	—	Schucht
1·95	0·99		—	15·43	4·40	33·68	—	—	A. Grimm
—	—	—	—	9·75	1·24	21·29	14·02	—	Anderson

Geographical Distribution of Phosphate of Lime and

Localities.	Longitude of Greenwich.	Latitude.	Designation.	Analysis. Water.	Analysis. Loss on Ignition.	Analysis. Lime.
19. *Peru.*	Degrees.	Degrees.		Per Cent.	Per Cent.	Per Cent.
Lobos de Tierra (Isle) .	82 W.	6·5 S.	Guano . . .	23·79	—	18·91
Lobos de Afuera (Isle) .	81 W.	7 S.	,, . . .	19·60	—	—
Macabi ,, (Isle) .	81 W.	7·5 S.	,, . . .	30·33	—	—
Guanape ,, (Isle) .	79 W.	8·5 S.	,, . . .	25·88	—	—
Chinchas (Isle) . .	77 W.	13·5 S.	,, . . .	—	—	10·99
Ballestas (Isle) . .	76·5 W.	13·5 S.	,, . . .	14·87	—	—
Independencia Bay .	76 W.	14 S.	,, . . .	13·22	—	12·59
20. *Chili.*						
Pabellon de Pica . .	70 W.	21 S.	Guano . . .	13·05	—	14·23
Punta de Lobos . .	70 W.	21 S.	,, . . .	14·12	—	—
Huanillos . . .	70 W.	21·5 S.	,, . . .	14·12	—	—
Mejillones . . .	71 W.	23 S.	Phospho guano .	4·44	—	37·64
Angamos . . .	71 W.	23 S.	Guano . . .	7·39	64·81	5·11
Corcovado . . .	73 W.	43 N.	,, . . .	18·19	—	13·67
E. Pacific Ocean.						
21. *Sporadic Isles.*						
Fanning (Isle) . .	159 W.	4 S.	Phospho guano .	8·00	12·32	42·84
Jarvis (Isle) . . .	159·5 W.	0·5 S.	,, ,, .	12·118	5·992	34·83
Malden (Isle) . .	155 W.	4 S.	,, ,, .	4·78	5·18	46·229
Starbuck (Isle) . .	156 W.	5·5 S.	Guano in crusts .	10·01		44·96
22. *Phœnix Group of Isles*						
Mary (Isle) . . .	171·6 W.	2·75 S.	Phospho guano .	5·63	—	44·40
Enderbury (Isle) . .	171 W.	3 S.	,, ,, .	8·76	8·81	40·76
Phœnix (Isle) . .	170·45 W.	3·5 S.	,, ,, .	4·93	8·66	44·91
Sidney (Isle) . . .	171·50 W.	4·5 S.	,, ,, .	7·38	7·59	42·96
23. *Gilbert Group of Isles.*						
Ocean (Isle) . . .	169 E.	1·5 S.	Phosphate . .	1·01	2·7	49·5
24. *Baker Isles.*	176·25 W.	0·13 S.	Phospho guano .	3·945	7·758	43·379
Howland (Isle) . .	177 W.	0·5 S.	,, ,, .	5·34	—	44·48
F. Australia and Australian Isles.						
25. *Australian Continent.*						
Shark's Bay . . .	114 E.	26 S.	Phospho guano .	15	—	—

Guano Deposits and their Chemical Composition—continued.

Analysis: Lime not Combined with P_2O_5.	Analysis: Oxide of Iron.	Analysis: Alumina.	Analysis: Magnesia.	Analysis: Phosphoric Acid.	Nitrogen.	Tribasic Phosphate of Lime.	Carbonate of Lime.	Calcium Fluoride.	Analyst.
Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	
—	1·89		0·27	17·54	5·58	—	—	These Guanos contain 2·5 % Potash.	Anglo-Cont. G. W.
—	—	—	—	16·70	3·60	—	—		
—	—	—	—	11·95	11·05	—	—		Ohlendorff & Co.[1]
—	—	—	—	12·25	11·0	—	—		,,
—	0·30	—	1·19	13·52	14·39	—	—		,,
—	—	—	—	12·23	12·50	—	—		,,
—	1·52		0·39	10·89	7·68	—	—		Anglo-Cont. G. W.[1]
—	2·73		0·20	12·78	8·88	—	—		,,
—	—	—	—	15·10	5·70	—	—		,,
—	—	—	—	13·30	6·60	—	—		
0·12	0·66	0·90	2·90	31·72	0·59	69·24	—	—	A. Grimm
—	0·88		1·11	7·13	19·28	—	—	—	Anderson
—	0·20		1·17	15·14	10·52	—	—	—	Anglo-Cont. G. W.
—	—	—	0·61	34·16	—	74·57	—	1·01 fluor.	H. Gilbert
—	0·09	—	0·568	17·67	0·647	38·57	—	—	V. Liebig
—	—	—	—	34·75	—	75·86	8·29	—	Völcker
—	—	—	—	40·12	—	87·58	—	—	,,
9·89	0·23		—	29·26	0·54	63·87	—	—	A. Grimm
—	—	—	—	28·74	0·38	62·74	16·50	—	Völcker
—	0·23		—	36·10	0·63	70·80	4·54	—	
—	0	0	2·03	34·41	0·28	75·13	6·0	0·82	H. Gilbert
3·19	0·42		—	38·73	—	84·65	4·91	1·0	V. Grueber
—	0·067	—	2·207	40·329	1·35	88·03	—	—	V. Liebig
2·29	0·18		—	29·75	0·53	64·94	—	—	A. Grimm
—	—	—	—	23·59	—	50·53	4·6	—	

[1] Same firm.—Tr.

Geographical Distribution of Phosphate of Lime and

Localities.	Longitude of Greenwich.	Latitude.	Designation.	Analysis. Water.	Loss on Ignition.	Lime.
26. *Australian Isles.*	Degrees.	Degrees.		Per Cent.	Per Cent.	Per Cent.
Brown (Isle) . . .	123·5 E.	14 S.	Phospho guano .	15·00	10·30	39·94
Jones (Isle) . . .	126 E.	13 S.	,, ,, .	7·93	10·92	42·86
Lacepedes (Isle) . .	122 E.	17 S.	,, ,, .	6·78	10·54	41·33
Abrolhos (Isle) . .	113 E.	28 S.	,, ,, .	4·48	—	43·20
,, ,, . .	—	—	,, ,, .	10·10	6·20	—
Huon (Isle) . . .	163 E.	18 S.	,, ,, .	9·74	19·90	37·60
Bird's (Isle) . . .	156 E.	22 S.	,, ,, .	10·70	9·70	—
Bat (Isle) . . .	146 E.	3 S.	Guano . . .	14·53	—	14·64
G. Asia.						
27. *Palestine.*						
Country East of Jordan .	35·5 E.	32 N.	Phosphorite . .	—	—	—
28. *Arabia.*						
Kurian Murian (Isle) .	56 E.	17·5 N.	Phospho guano .	8·70	9·30	—
29. *Malay Archipelago.*						
Timor (Isle) . . .	124-127 E.	8-10 S.	Phospho guano .	6·25	—	40·33
Christmas (Isle) . .	105·5 E.	10·5 S.	Phosphate . .	3·05	—	—
H. Africa.						
30. *North Africa.*						
Algeria	3 E.	37 N.	Mineral phosphate .	2·39	—	50·10
Tebessa	8 E.	35·5 N.	,, ,, .	1·97	—	50·30
Toqueville	8 E.	36 N.	,, ,, .	0·77	—	—
Tunis	10 E.	37 N.	,, ,, .	5·95		45·35
Sfax	10·5 E.	34·5 N.	,, ,, .	—	—	—
Gafsa	9 E.	45·4 N.	Phosphate . .	2·6	2·99	45·12
Egypt	29 E.	31 N.	Bat guano . .	17·19	29·50	—
31. *South Africa.*						
Damaraland	14 E.	22 S.	Guano . . .	18·89	—	12·4
Ichaboe (Isle) . . .	15 E.	26·5 S.	,, . . .	17·97	17·0	—
Saldanha Bay . . .	18 E.	33 S.	,, . . .	17·04	—	24·26
Algoa Bay	26 E.	34 S.	Phospho guano .	20·25	12·10	—

Guano Deposits and their Chemical Composition—continued.

Analysis.									
Lime not combined with P_2O_5.	Oxide of Iron.	Alumina.	Magnesia.	Phosphoric Acid.	Nitrogen.	Tribasic Phosphate of Lime.	Carbonate of Lime.	Calcium Fluoride.	Analyst.
Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	
—	0·32	—	0·21	31·40	—	68·54	—	0·34 fluorine	H. Gilbert
2·38	0·33	0·54	—	34·22	—	74·70	4·25	—	A. Grimm
—	1·61	—	0·55	35·22	—	76·88	—	traces	Cherson
5·56	3·10		—	—	0·38	69·46	—	—	A. Grimm
—	1·67		0·97	33·67	—	70·32	—	2·57	H. Gilbert
—	0·24	—	0·09	28·59	1·16	62·41	—	traces	Chevron
—	—	—	—	—	1·24	23·15	36·45	—	Anderson
—	0·40	0·57	—	7·30	7·54	15·94	6·97	—	Völcker
—	0·64	0·48	traces	38·24	—	83·68	—	9·8	Elschner
—	—	—	—	26·24	1·37	57·30	—	—	Huson
3·49	1·48		—	31·14	0·82	67·98	6·23	—	A. Grimm
—	0·71	1·22	0·26	39·18	—	83·53	4·82	3·44	H. Gilbert
14·09	0·53		—	30·44	—	66·45	—	—	A. Grimm
—	0·55		0·50	28·16	—	61·47	20·19	—	A. Retter
—	0·98		0·81	26·32	—	57·46	22·80	-	,,
—	0·81	0·62	0·6	27·25	—	59·48	11·52	—	Schucht
—	1·2	0·6	—	27·2	—	59·0	14·0	-	?
—	1·68		0·5	27·23	—	59·44	11·95	—	Schucht
2·76	—	—	—	—	11·81	—	—	—	Völcker
—	—	—	—	13·40	8·88	29·25	—	—	A. Grimm
—	—	—	—	11·19	—	24·44	—	—	Anderson
—	2·27		0·97	24·52	1·41	55·40	—	—	H. Gilbert
—	—	—	—	6·68	0·43	14·60	—	—	Grouven

CHAPTER III.

DRYING AND ENRICHMENT OF PHOSPHATES.

Drying.—Phosphates, to fulfil the conditions required of them, must be dried and finely ground. When the phosphates are massive (rock phosphate) or in lumps, they may be completely dried in summer by storage in a warehouse with vents in the side; in winter, the drying is accomplished in a drying machine. Formerly phosphates were calcined to increase the percentage of phosphoric acid and facilitate grinding (p. 86 *et seq.*). Drying is indispensable in the case of the sandy phosphates of Mons, Somme, and Cambresis. This operation is conducted in a kiln, on cast-iron plates, about two fifths of an inch thick, in contact with the flames of one or more furnaces but protected from overheating. The phosphate is spread on these plates in layers of 4 to 5¾ inches thick, according to the nature of the material. The drying reduces this thickness about one-third. A charge is finished in 6 hours over the flues above the flames; in 8 hours on the flues, forming the first circuit of the flames; and in 10 to 12 hours on the flues, forming the second and the third circuit. A drier of 250 square metres (820 square feet) will suffice for treating 35 to 40 tons of dry phosphate per day of 24 hours. The consumption of coal is about 2 cwt. per ton of the granular roasted material obtained. The product, so dried, passes into cylindrical sifting machines, polygonal in section like those of an ordinary flour mill covered with wire gauze Nos. 70, 80, 90, 100, 110 and fitted with baskets inside, in which to collect the larger fragments. The dry sand passes successively through the different mesh sieves, commencing with the larger sizes. The exit of the products is thus regulated in a uniform manner over the whole length of the apparatus. The residues on the sieves pass out at the ends of the reels and are crushed in flat stone mills running at a speed of 100 revolutions per minute. Each pair of stones absorbs 6 to 7 H.P. The sifted phosphate is generally 7 to 8 per cent richer in tribasic phosphate than the ground phosphate; the whole is mixed in order to produce one average quality of the appearance of finely ground pepper. When the phosphate is in nodules, as in Auxois, they must be crushed or cracked before grinding. The crushers and cracking machines,

used in the Meuse and Ardennes, consist of two cast-iron cylinders, studded with projecting teeth in the form of pyramidal projections, which mutually intersect each other. At other times the crusher consists of a grooved moving plate which crushes the phosphate against a fixed plate (see Fig. 12 and context). When the nodules to be crushed are not quite dry, the heat caused by the friction in the mills produces steam, which finds an exit through wooden pipes fitted either to the boxes which collect the ground phosphate, or to the mill covers. These pipes, acting as evaporators, pass through the roof. The steam carries with it some of the fine phosphate dust. Of late mechanical driers have been installed for drying raw phosphates.

Calcining the Nodules.—Before crushing the nodules, they were at first only dried in the sun, or on iron plates heated artificially. More recently they have been calcined in special furnaces to free them completely from water and carbonic acid; their weight per cubic meter is thus reduced from 1000 kg. to 950 kg., say from 20 cwt. to 19 cwt., the percentage of phosphoric acid being increased *pro rata*. These furnaces are 4·5 metres, about 14 feet 9 inches high, and about 25 cubic metres in capacity, with a diameter of 2·65 metres, say 8 feet 8 inches, at the top, 1·8 metres, say 5 feet 11 inches, at the base, and 3 metres, say 9·84 feet, in the centre. The bottom consists of a busk formed by two inclined planes ending in two wide discharging orifices. The phosphate rests on iron bars, supported at one of their ends by the inclined planes of the busk and at the other by the horizontal metallic lintels which form the crown of the discharging orifice. These bars form two grates at the bottom of each furnace, and they are used to regulate the descent of the products. It suffices to draw one to let the calcined nodules fall through the opening. They can thus be withdrawn at any point of their contact with the grate; above each grate the side of the furnace is pierced by an opening through which to inspect the progress of the operation. The furnaces are built of bricks or masonry; they are filled with nodules in layers 4 inches thick which are separated by very thin layers of fuel, small coke, or anthracite. A furnace of the above dimensions yields 4¼ cubic metres of calcined phosphate in twenty-four hours. A charge thus remains in the apparatus five to six days. The roasting of a ton of nodules requires about 1 cwt of fuel. The nodules first go to a crusher with smooth blades; they then pass by an elevator chain of cups to the top of the building where they are dropped into an iron trough which feeds the mills beneath. The ground phosphate passes automatically to an elevator which raises it to the level of the two sifting machines between which it is fed. From the sifting machine the substance falls into a wooden reservoir fitted with two bag filling machines. Whilst in the Pas de Calais district

phosphates are always washed after simple hand sorting from the bulk of the gangue, in the Meuse and Ardennes they are now—after disintegration by the pick and breaking up on the spot—screening them by throwing them on a trellis of iron wire called a *billard*, the square meshes of which are 8 to 20 mm., or a screen of iron bars 8 to 10 mm., say one-third to two-fifths inch apart, which frees them from one-third to one-half of their impurities, but at the same time small nodules and fragments broken off by shock are lost. This method is profitable when the nodules are not friable, and easily separated from their gangue. Screening is followed by washing with a current of water in mechanical washers, or in washers fitted with blades, or dry sorting known as *fanage*. The phosphate nodules occur near the outcrop of the Greensand at no great depth, the sock of the plough often bringing them to the surface. An extensive business is done in collecting them and selling them in bulk to the phosphate cleaners. Fanage consists in passing the raw material through a screen after exposure to the air, so as to dry it completely and thus render the argillaceous sands more easily separated from the nodules. The operation is repeated five or six times with the object of getting a satisfactory cleaning. Drying is facilitated by spreading the nodules in a thin layer on the ground and turning them like hay, from which operation is derived the name given to the process. Fanage only succeeds if the gangue is of such a nature as to lend itelf to the treatment. The *nodules fanés*, poorer than washed nodules, contain 10 to 15 per cent of impurities. They are exposed to rain to wash the impurities away in the form of mud. Fanage is completed by rapid washing.

Sorting and Sale of Raw Phosphates.—Raw phosphates are sold by P_2O_5 content. They are bagged up into 5 grades each differing by 5 units—50-55, 55-60, 60-65, 65-70, 70-75, 75-80 per cent. It is thus easy to supply any strength required. To control the strength of wagon loads, buyer's and seller's agents take counter sealed samples at the station from each wagon, four random samples from 25 to 30 bags. One is tested by the seller's chemist, the other by the buyer's. When there is more than 2 per cent difference between the results, the third sample is analysed by a third chemist and the average of the nearest taken. The fourth sample is kept as a check. In case of shipment the goods are sampled in the wagons as they reach the harbour. Sampling is done either by the broker alone or by the broker in the presence of the seller's agent.

Different Methods of Strengthening and Utilizing Poor Quality Phosphates.—Numerous methods have been suggested to utilize the large quantities of low-grade phosphates unfit for making superphosphates. These methods may be specified as follows: (1) To

fortify them in various ways; (2) To free them from the sesquioxides of iron and alumina, or (3) To increase their solubility or to extract from them their phosphoric acid. None of these processes have been adopted in actual practice, because they are too costly and also incompatible with the present state of the manure trade; they will continue in abeyance as long as high grade phosphates, with a low oxide of iron and alumina content, are available, the latter only requiring to be rendered soluble to produce excellent superphosphates. The following are the chief patents taken out for this purpose:—

1. *Dumonceau and Nicolas* (French patents Nos. 201,427 and 201,461) propose to fortify low-grade phosphates, consisting of phosphate of lime, and carbonate of lime, by the use of sulphur. The principle of the two methods is as follows: Phosphatic chalk is calcined so as to produce a mixture of phosphate of lime and quicklime, which is mixed with water and sulphur in iron pans. The insoluble phosphate of lime is separated from the soluble sulphides formed. The strength is thus fortified 20 to 30 per cent. A current of carbonic acid is injected into the solution, sulphur and sulphuretted hydrogen being thereby separated, the latter being converted into sulphur by means of sulphurous acid.

2. *Simpson* replaces sulphur by sulphuretted hydrogen (German patent 58,925), and after calcination of the raw phosphates, injects it into water, holding the phosphates in suspension. The calcium sulphides are afterwards treated with carbonic acid, or with sulphate of soda, to transform them into gypsum and sodium sulphides; the latter treated with carbonic acid yielding sulphuretted hydrogen and soda.

3. *Brochon* (French patent 215,577) extracts phosphates rich in carbonate of lime by means of carbonic acid under pressure after crushing and stirring up with water. The liquid containing the acid carbonate of lime is separated from the insoluble phosphate and treated for the recovery of the carbonic acid. Carbonate of lime is, however, only slightly soluble in carbonated water even under pressure (1 cubic metre of water only dissolves 3 kg. or 100 gallons, 3 lb. under a pressure of 4 atmospheres at 5° C.). The process is thus too costly.

4. *Winsinger*, to prepare bicalcic phosphate free from oxide of iron, completely soluble in citrate of ammonia (German patent No 51,739), extracts all the phosphoric acid of the phosphate of lime by sulphuric acid, converts half the solution into monocalcic phosphate, by addition of carbonate of lime and milk of lime, which precipitate the iron; he adds this precipitate to the other half, and obtains by addition of sodium sulphate, sodium carbonate and quicklime, phosphate of lime insoluble in water free from oxide of iron, which he finally adds to the solution of monocalcic phosphate.

A bicalcic phosphate is thus obtained, and gypsum and caustic soda are produced as bye-products. This process is rather complicated.

5. *O. Iahne* (German patent 57,295) prepares phosphate of lime free from oxide of iron, alumina, and silica, by acting on phosphates rich in oxide of iron and alumina with sodium bisulphate. The raw phosphates (coprolites, etc.) treated with an aqueous solution of sodium bisulphate, in this case carbonate and phosphate of lime, dissolve, whilst the silica, and iron, and alumina compounds remain insoluble, and may be separated by filtration along with the gypsum. By evaporating the solution a yellow salt is obtained, the composition of which corresponds to the formula $2Na_2SO_4 + CaH_4P_2O_8 + H_2O$, which may be employed as such, as a manure, or mixed with gypsum, horn meal, or peat; it may also be used in stables, to fix ammonia.

6. In making superphosphates, *Martin* proposes to use the acid sulphate from the manufacture of nitric acid. The acid sulphate from the cylinders is dissolved in water, so as to produce a solution of 45° to 50° B. The precipitate consists of bisulphate, which it is easy to convert into sulphate by recrystallization, whilst the strongly acid solution is used to dissolve raw phosphates. All the phosphoric acid is dissolved, and the resultant superphosphates have less tendency to retrograde than those made with sulphuric acid of 50° to 53° B.

7. *Thonnar and Huxton's* Belgian patent No. 96,109, and *Rolland's* Belgian patent 196,190, to eliminate the oxides of iron and alumina, may also be mentioned.

8. *Schucht* proposed to make superphosphates from ferruginous phosphate thus: As soluble ferric oxide induces retrogradation of the phosphoric acid in superphosphates, whilst the ferrous oxide is inactive, and as sulphate of ammonia possesses the property of forming with a ferrous salt double salts very stable in air, Schucht, on such data, proposed to dissolve phosphates in presence of sulphate of ammonia, then to effect the reduction and so obtain very stable superphosphates of ammonia. With this end in view, the finely ground superphosphates are mixed with sulphate of ammonia. One part Fe_2O_3 requires 1·75 parts of that salt to form the double salt $FeSO_4 + (NH_4)_2SO_4 + 6H_2O$. Reduction can only be effected by weak sulphurous acid which is injected under pressure into the diluted mixture of superphosphate heated to 80° to 100° C. Schucht believed that the small amount of sulphurous acid in the product would quickly oxidize and become innocuous to plant life. The author is not aware if this method has ever been used; in any case, Schucht makes no mention to this effect in his book. Besides, a phosphate containing 3 to 4 per cent of ferric oxide and alumina will only cause an inversion of 0·50 per cent in stored superphos-

phate, a loss say of 1d. a cwt. That is why the above process only merits attention, in those cases where the purchaser also pays for the nitrogen. Otherwise the process would hardly be worth the trouble.

9. *Carr's* process, dealing with phosphates rich in oxides of iron and alumina, is analogous. It consists in calcining the phosphate, grinding it fine and then mixing 1000 parts with 400 parts of sulphate of ammonia dissolved in 400 c.c. of hot water, to which is then added 800 parts of sulphuric acid of 53° B. A violent reaction ensues, the mass intumesces and heats to 110° C. After an hour it solidifies and is easily ground; it contains 18 per cent of phosphoric acid, two-thirds of which are soluble in water. This process is interesting, moreover, it is simple, and yields good results; it might be advantageous to use it in the manufacture of phosphate of ammonia, if the raw materials were to be obtained cheaply. Besides, this process seems to preclude the retrogradation of the soluble phosphoric acid.[1]

10. *Glaser* proposes to manufacture precipitated phosphates from insoluble phosphates of alumina, by treating the latter with a cold alkaline solution or with a hot concentrated solution of alkaline carbonate. In this operation the phosphate of alumina is dissolved. In using the alkaline solution, the liquid separated from the residues is treated with carbonic acid. If a hot solution of alkaline carbonate be used, it is cooled, and the dissolved phosphate of alumina is precipitated. The solution is then used for a new operation. But from tests made, raw phosphate of alumina does not dissolve in a hot solution of alkaline carbonate.

11. *Petermann* of Gembloux recommends treating the raw phosphate at a high temperature, to convert the phosphoric acid into a very soluble form. Bazin has based a British patent No. 15,237 on this principle. He heats phosphates in retorts to a temperature of 1300° to 1500° C.

12. *Hodgkins* (American patent No. 423,320, 1890) mixes the phosphate in fine powder, with quicklime, which he then slakes. But it is not apparent how such treatment can render phosphates more soluble. Besides, no field experiments appear to have been made to test the value of the resultant manure.

Manufacture of Precipitated Phosphate by Electrolysis.—A new method of manufacture, based on electrolysis, has been invented by Prof. W. Palmer of Stockholm. It consists in converting the raw phosphate by the wet way into a readily assimilable form, at the ordinary or a slightly elevated temperature. The raw

[1] But it is evident on the face of it that such generalizations are futile. The data given can only have been applicable to the particular phosphate to which Carr applied it. All phosphates rich in oxides of iron and alumina would not respond to such treatment so as to yield the above results.

material is ground apatite, which need not be finely ground. In an apparatus, specially constructed for the purpose, a solution of chlorate or perchlorate of soda is electrolyzed; this disengages free chloric acid, sometimes even perchloric acid, in the *anode* cell. The acid *anode* liquid is made to react on the raw phosphate in a battery of wooden cases, fitted with perforated bottoms, so that the solvent first comes in contact with almost exhausted apatite. The alkaline liquid from the *cathode* is added to the saturated solution, in special precipitation vats, taking care to stir, until a slightly acid reaction ensues. There is thus formed a crystalline precipitate of acid phosphate of lime. It is freed as completely as possible from the mother liquor, by filtration and washing, which is greatly facilitated by the physical nature of the phosphates. The yield is very satisfactory, because only about 1 per cent of the phosphate in the raw material remains in the solution. The latter, which contains a third of the amount of lime originally eliminated from the apatite, is mixed with the residual alkaline cathode liquid, when the greater part of the lime is precipitated as hydrate; finally, a current of carbonic acid gas is injected. After precipitating the lime the solution is withdrawn and run into the electrolyzer. The electrolyte is thus continuously regenerated. The product so obtained generally contains 36 to 38 per cent of total phosphoric acid (the formula $CaHPO_4 + 2H_2O$ requiring 46·07 per cent of P_2O_5). About 95 per cent of the phosphoric acid in this product is soluble in Petermann's solution of ammoniacal citrate of ammonia. The composition of the product depends, moreover, on the amount of lime in the raw material; when it is rich in lime it requires a greater amount of acid, and consequently of electrical energy. There is a bye-product of slaked lime equal to 33 per cent of the bicalcic phosphate formed. This process, which was the subject of several years' laboratory work, was tried industrially a few years ago in an installation of 6 to 8 electric horse-power. One electric horse-power can produce annually 20 cwt. of bicalcic phosphate soluble in citrate, or 23 cwt. of 32 per cent. The cost of manufacture has been provisionally estimated at 8·44 Swedish crowns per cwt. These figures refer to an annual production of 2200 tons of bicalcic phosphate of 34 per cent. Comparative experiments on oats cultivated in pots, and continued for five years, showed that the phosphate precipitated by electrolysis, provided that its composition responds to that of bicalcic phosphate, exerts a fertilizing action fully equal to and as durable as superphosphate. The addition of substantial amounts of carbonate of lime did not diminish the assimilability of the former, whilst with tribasic phosphate the contrary is the result.

CHAPTER IV.

HISTORICAL REVIEW OF SUPERPHOSPHATE MANUFACTURE.

It can be safely asserted that the superphosphate industry is the outcome of Liebig's theory. He was, in fact, one of the first to recommend restoring to the soil, not only the nitrogen removed by crops, but also the mineral matter, more especially the phosphoric acid. For this purpose he recommended the use of bone dust, and also of phospho guanos. But having remarked that the phosphoric acid of these substances acted very slowly, he advised that they should be treated with sulphuric acid so as to render the phosphoric acid soluble, and immediately assimilable by plants. His method was adopted, and yielded remarkable results, thus giving birth to the superphosphate industry which spread rapidly in Germany, Great Britain, and France.[1]

The Manufacture of Superphosphates from 1850 to 1870.—It is interesting to follow the new industry in the different phases of its evolution. The theory of superphosphate manufacture is in itself very simple. Raw phosphates contain phosphoric acid, as tribasic phosphate of lime, insoluble in water, and consequently not assimilable by plants. The task of the manufacturer of superphosphate consists, therefore, essentially in converting the insoluble phosphoric acid of raw phosphates into water soluble or citrate soluble phosphoric acid. This is done by treating them with sulphuric acid, which removes as gypsum two parts of the lime with which the phosphoric acid is combined, leaving one part of the lime combined with the phosphoric acid, as the monobasic or acid phosphate of lime soluble in water. The product so converted

[1] The writer has no intention of disparaging Liebig's claim to the treatment of bones by acid; but the treatment of coprolites and mineral phosphate by acid was first suggested by the Rev. Mr. Henslow. Mr. Lawes was either present at Mr. Henslow's lecture or read a report of it; he took out a patent for the process and proceeded against Mr. Purser for digging for coprolites on his (Mr. Purser's) own land for the purposes of treating them by acid so as to dissolve them. Long litigation ensued, which was afterwards settled amicably. Lawes established a factory at Deptford and Purser at Millwall, with the river Thames between them. Purser's Millwall factory was closed in the early nineties. Lawes' manure factory is now at Barking. The mineral superphosphate industry is a British-born industry, like the sulphuric acid manufacture.—Tr.

is called superphosphate, since it contains more phosphoric acid than the normal phosphate.

As regards the simplicity of the process, the installations of the first superphosphate factories were very primitive. They contained little or no machinery. Three sheds, one to cover the raw phosphates, the other the den in which to dissolve the phosphate, and the third for storing the superphosphate. So much for the factory. The tools in the beginning consisted of a few harrows, hoes, rakes, and a sieve called a screen—that was all. As to the indoor installation, it included a sulphuric acid tank, a few lead-lined measuring tanks, and three or four rectangular, round, or square dens. These dens were first made of brick steeped in boiling tar; afterwards cast-iron cases one inch thick, and sunk in the ground, were used. The method of manufacture was the following: A certain amount of sulphuric acid of 50° to 52° B. was run into the den; at the same time the phosphate was weighed and heaped on the edge of the den. Three men, each armed with a rake, agitated the acid, whilst the third gradually shovelled in the phosphate. The mass soon thickened, and even set before the "mixing" was complete. Nevertheless, to obtain a homogeneous mixture the mass was triturated by bringing it from one side of the den to the other; finally it was filled into barrows and removed into the superphosphate shed. There it lay in heaps for a month; finally it was hand screened and sent out to customers. When well dissolved, it gave no core, any lumps being crushed by the back of the shovel, until sufficiently fine to pass through the screen. By such simple means sufficiently dry superphosphates were obtained, comparatively fine and well dissolved. These methods sufficed at that time, because the very pure raw phosphates were delivered in the ground state, or at least sufficiently fine to pass through the screen.

1871 *to* 1880.—During this period the raw phosphates used, included spent bone black from sugar works, and guano from the Pacific Islands, Baker, Jarvis, etc., were chiefly used. From 1871 Mejillones guano began to be used, and then the first difficulties in the manufacture were met with. The larger factories then installed flatstone mills, roller mills, or stamp mills. This equipment, however, soon became inefficient when it was a question of working mineral phosphates such as Canadian or Norwegian apatite, Sombrero, Navassa, Curaçoa and Aruba phosphates, Mexican guano, rock phosphate, bone ash, etc. Powerful crushers were then added to the flatstone mills, for it was realized that fine grinding then became essential in dissolving the phosphate, and in drying the superphosphate. At the same time, a mechanical crusher and sifter for the superphosphate appeared desirable. It was thus that the crusher called Carr's disintegrator was adopted. This machine did not at first always and everywhere give the result expected;

the superphosphates, unless suitably dissolved, were converted into paste. Such was the state of affairs about 1880. But to follow up the treatment of the phosphates: At the outset of the manufacture of superphosphate, the manufacturer was himself his own chemist; he submitted his raw phosphates to a series of dissolving experiments, varying the quantity of acid each time. He then sent samples to an analyst of the superphosphates which appeared to have succeeded best, then he applied to the stock of phosphates the treatment established by groping in the dark. Each new raw material required fresh experiments. It is hardly necessary to remark that such a method of working was fertile in disagreeable surprises for the manufacturer. This remark may have applied to continental manufactories but it would be possible to name several British manure manufactories the work of which was controlled by chemists 15 to 20 years prior to 1871, and flat stone mills were also in use prior thereto. The translator has handled works laboratory journals of the early fifties, which show the manufacture was even then under strict chemical control by qualified men on the spot. British manure patent literature of the earlier days speaks for itself.

1880 *to* 1894.—In spite of the good quality of the raw phosphates, and their low percentage of oxide of iron and alumina, hitches in manufacture were frequent, and gradually the need was felt for a permanent control. Thus, since 1880, factories of any importance have each a chemist whose duty it is to follow the material throughout all the phases of its treatment. This control became more urgent when it was observed in some kinds of mixed manures that a certain amount of the phosphoric acid had retrograded, that is to say, it had returned to the condition insoluble in water. At the same time that in using the Canadian and Norwegian apatite, and Florida and other mineral phosphates, chlorine and fluorine compounds highly injurious to the health of the workmen, and annoying to the neighbourhood, were evolved. The machine for mixing the acid with the phosphate was then substituted for the treatment in the open den. The first machine of this nature was an inclined cylinder, in which a shaft fitted with blades arranged in a helical manner revolved; it was charged with acid and phosphate at the upper end, and the mixture was run out at the lower end. Afterwards this apparatus was replaced by a flat mixer of cast-iron, likewise furnished with an agitator, in which the acid and phosphate were agitated two or three minutes, then run out into a truck underneath, whilst the gas given off by the phosphate was carried to the open air above the roof through a wooden chimney. These machines answered all requirements so long as only guano or other phosphates rapidly attacked by sulphuric acid were being treated; however, the products were generally deficient in porosity because the greater part of the carbonic acid was disengaged owing to the material remaining

too long in the mixer. Then the system of closed chambers or dens was adopted, because in dissolving very hard mineral phosphates, such as Canadian apatite, pebbles, Florida phosphate, etc., a higher temperature was required, which it was easier to attain and maintain in the closed chamber, where the superphosphate remained for about twelve hours; further, in connecting it with a well-constructed flue for the disengagement of the acid vapours, the health of the workmen was safeguarded. When the chamber possesses two flues for the disengagement of gas, each 1 metre (3·28 feet) wide, and these flues are each fitted with a fan, and can be put in connexion with the chimney stack of the factory, or with a condensation plant, it is easy to eliminate steam and acid gases. A drier superphosphate is thus obtained, and during the emptying of the chamber or "house" the workers can enter without running the risk of getting "gassed". But in actual practice difficulties are frequently met with. As already mentioned, as far back as 1880 it was necessary to instal plant to condense the gaseous chlorine and fluorine compounds; these consisted mostly of wooden or masonry towers drenched with water, by a Koerting's vaporizer. The hydrofluosilicic acid obtained under these conditions can be converted into silico-fluoride of sodium, the selling price of which covers the cost of condensation, leaving even a slight margin. This product, unfortunately, has only a limited use as a preservative. The mixer installed above the closed "dens" or "houses" is that of Lorenz, which is universally used on the Continent. Lately, dissolving chambers have been installed raised above the floor level, and belt conveyers pass underneath to facilitate emptying. This system has been adopted by certain factories.

1895 *to* 1908.—Such was the situation from 1880 to 1894. Superphosphate factories possessed mills, machines for mixing acid with phosphate, installed above a close den, into which the mixture was discharged and left to itself for twelve hours; arrangements for elimination and condensation of acid gases, disintegrators, or roller mills, armed with teeth for grinding superphosphates. Meanwhile ball mills appeared, then ball mills combined with tube crushers, then Griffin's pendulum crusher, etc.; dust chambers, on different plans, were installed; new systems of transport, such as aerial conveyors, belt conveyors, to bring the phosphate to the crushers, coal to the boilers, the crushed and screened superphosphate to the storehouse. The adoption of aerial conveyors marks an important development in the superphosphate industry, for independently of the economy in hand labour, they enable the superphosphates to be thrown on the heap from above, thus ensuring the proper preservation of the product. It is closely connected with electricity, the ingenious applications of which allow the use of mechanical equipment in all parts of the factory, in many parts of

which it would be impossible to erect shafting. Electricity and aerial conveyers form a sort of connecting link between the different appliances in the factory, contributing greatly to their increased output. Electric light diffuses cheerfulness in all directions; the electric motors driven from a central station work silently in the most distant parts of the factory, the different organs of which thus work in perfect harmony. A most important question is that of judging the treatment to which superphosphates should be subjected from the moment it is shifted from the den, so as to obtain in the most simple and the most rapid manner a good product which will keep well. With the object of solving this problem, numerous processes have been elaborated, all converging to the same end, which is to secure a dry pulverulent phosphate easily distributed by the drill sowing machine. The origin of these researches dates from the time when Florida phosphate was first used, which from 1890 was and still is one of the most important raw materials of superphosphate factories, afterwards the phosphates of Tennessee, Algeria, and Tunis. Superphosphates made from Florida phosphate are distinguished by a high percentage of free phosphoric acid which attracts moisture from the atmosphere and keeps the material damp. The simplest means of remedying this inconvenience consist in drying them, and thus quite a series of driers have been constructed for the purpose. At the present time all superphosphates, and especially those intended for export, are dried. But it was soon observed that if drying diminished the percentage of moisture in the superphosphate, it increased the percentage of free phosphoric acid, and of hydrofluosilicic acid, and in such conditions, whilst appearing dry, they possessed the property of attracting moisture and attacking the canvas of the bags. Steeping in gum kino extract was, however, found in Australia to render manure bags rot proof. In 1896 it was discovered that degelatinized bones, and more recently Gafsa phosphate, afforded simple means of drying superphosphates and rendering them pulverulent without exposing them to retrogradation. This point will be reverted to in the sequel. At the same time several specialists in this industry, independently of each other, have endeavoured to find methods for obtaining good superphosphates whilst imparting great rapidity to the working process. In this way the grating machine was invented (Heymann and Nitsch's process). But experience proved that perfect results could be obtained only by finely dividing the superphosphates from the mixing den and by diminishing its free acidity. This result has been fully realized. Owing to improved equipment, means are available for producing from any raw phosphates, superphosphates which answer all requirements, since it has been recognized that dryness and the pulverulent state of the superphosphates depends, in the first place, not on their percentage of moisture but on their

free acid content. The recently discovered phosphates of Christmas Island and Ocean Island enable phosphates with 20 to 21 per cent of phosphoric acid soluble in water to be produced. Thus, as already observed, it is Florida phosphate which has been the occasional cause of the troubles in working which we have just enumerated. This same phosphate more than any other has been a most difficult problem to the chemists owing to its high percentage of oxide of iron and alumina, which are the great enemies of superphosphate manufacturers. The retrogradation of the soluble phosphoric acid brought about by the presence of these compounds have caused no end of trouble to the chemist and manufacturer, and if the means of prevention be not possessed by a factory working on the large scale, the causes and conditions under which they are produced have at least been determined. Chemistry, the inseparable companion of industry, has taken a considerable part in the progress realized in superphosphate manufacture from its birth to the present time. Chemists are attached to all manure factories; to them belongs the merit of freeing this industry from empiricism, and establishing it on a truly scientific basis. French chemists have had a large part in the development of the manure industry. Their learned researches joined to that of French geologists have greatly contributed to the realization of the value of the French phosphate deposits, the immense reserves of which will suffice for a long time to cover the requirements of French agriculture. That we in Great Britain have not a voluminous special literature dealing with the chemistry of manure manufacture, in no way detracts from the merits and claims of British agricultural and manure works chemists. Our Patent Office records prove that they have been first in the field in all branches of research in this domain. Both French and German current methods of precipitated phosphate manufacture, double superphosphate manufacture, and such like, are all borrowed from British patents like those of Professor Way, Benjamin, Tanner, etc., dating back to the sixties and seventies of last century.

CHAPTER V

THEORY OF THE MANUFACTURE OF SOLUBLE PHOSPHATES.

IT has already been seen that to render the phosphoric acid in raw phosphates soluble, when it exists as tribasic phosphate of lime, $Ca_3(PO_4)_2$, it suffices to replace the two atoms of dyad calcium by four atoms of hydrogen, which is done by means of sulphuric acid, the monobasic phosphate of lime, or acid phosphate of lime, $CaH_4(PO_4)_2$, soluble in water being produced, the calcium displaced by sulphuric acid forming gypsum, $CaSO_4 2H_2O$, according to the following equation :—

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 5H_2O = CaH_4(PO_4)_2H_2O + 2CaSO_4 2H_2O$$

Tribasic phosphate of lime.	Sulphuric acid.	Water.	Monocalcic phosphate.	Sulphate of lime.
310	196	90	252	344
	596		596	

As the equation shows, the sulphuric acid used is sulphuric acid which has not been concentrated, that is to say, it contains a certain amount of water incidental to its manufacture. This water assists in the crystallization of the two new compounds formed—monocalcic phosphate and gypsum—and at the same time helps in reducing the consistence of the mixing, thus facilitating decomposition. In fact, if the mass formed by the mixing of phosphate and acid be too thick, the new salts, especially gypsum, set and harden rapidly thus protecting a certain amount of the raw phosphate from coming in contact with the acid. Gypsum forms, so to speak, the skeleton of the superphosphate. But the conversion of raw insoluble phosphate into soluble phosphate is not accomplished in such a complete and adequate manner as the equation appears to indicate. Experiments have proved that the insoluble phosphate is rendered soluble in two somewhat parallel stages. The first, yielding free phosphoric acid and gypsum, extends only to two-thirds of the tricalcic phosphate. In the second the free phosphoric acid acts on the remainder of the tricalcic phosphate, combining with it to form acid phosphate of lime or monocalcic phosphate.

$$\underset{\text{Calcium phosphate.}}{3Ca_3(PO_4)_2} + \underset{\text{Sulphuric acid.}}{6H_2SO_4} + \underset{\text{Water.}}{12H_2O} = \underset{\text{Phosphoric acid.}}{4H_3PO_4} + \underset{\text{Tribasic phosphate.}}{Ca_3(PO_4)_2} + \underset{\text{Gypsum.}}{6(CaSO_4 2H_2O)} \quad (1)$$

$$\underset{\text{Phosphoric acid.}}{4(H_3PO_4)} + \underset{\text{Tribasic phosphate.}}{Ca_3(PO_4)_2} + \underset{\text{Water.}}{3H_2O} = 3[\underset{\text{Monocalcic phosphate.}}{CaH_4(PO_4)_2} + \underset{\text{Water.}}{H_2O}] \quad (2)$$

One can demonstrate the soundness of this equation by treating 310 parts of tribasic phosphate of lime with 196 parts of mono-hydrated sulphuric acid and 90 parts of water, diluting the mass rapidly with water and filtering quickly. Two thirds of the phosphoric acid are then present in the filtrate in the free state. But if the mass be diluted after it has set, all the phosphoric acid exists in the filtrate as monocalcic phosphate. The explanation lies in the fact that phosphoric acid is a much weaker acid, and acts more slowly than sulphuric acid; the reaction of equation (2) is therefore accomplished more slowly than equation (1). If an insufficient amount of sulphuric acid be used for conversion, only bicalcic phosphate is obtained :—

$$Ca_3(PO_4)_2 + H_2SO_4 + 6H_2O = Ca_2H_2(PO_4)_2,4H_2O + CaSO_4 2H_2O$$

In this conversion, a portion of the tribasic phosphate of lime is first transformed into monocalcic phosphate, $CaH_4(PO_4)_2$ which then reacts with the remainder of the tribasic phosphate of lime :—

$$\underbrace{\underset{252}{CaH_4(PO_4)_2,H_2O} + \underset{310}{Ca_3(PO_4)_2} + \underset{126}{7H_2O}}_{688} = \underbrace{2Ca_2H_2(PO)_2 2H_2O}_{688}$$

Free phosphoric acid, as previously stated, renders the superphosphate damp, pasty, and unfit for distribution (passing through the drill, etc.) in its raw condition. If the raw phosphate be rendered soluble, by hydrochloric acid or by nitric acid, no free phosphoric acid is obtained but merely the acid phosphate of lime, which is very soluble in water. Dry superphosphates can be obtained in that way. But such acids are less abundant and cost much more than sulphuric acid. Hydrochloric acid when it can be had cheap, is sometimes added in the proportion of 10 per cent to the sulphuric acid. But the phosphate is not rendered soluble by hydrochloric acid alone as that would give rise to calcium chloride, which is highly deliquescent, and cause the superphosphate to be damp and unsaleable. Moreover, calcium chloride is injurious to vegetation when present to any great extent. In presence of sulphuric acid any calcium chloride which may be formed is converted into calcium sulphate and hydrochloric acid, which latter assists in dissolving the phosphate.

From the following equation the quantities of sulphuric acid

and water required to dissolve a given amount of phosphate may readily be calculated :—

$$\underbrace{\underset{310}{Ca_3(PO_4)_2} + \underset{196}{2H_2SO_4} + \underset{90}{5H_2O}}_{596} = \underbrace{\underset{252}{CaH_4(PO_4)_2H_2O} + \underset{344}{2(CaSO_4 2H_2O)}}_{596}$$

In this connexion it will be well to bear in mind that the symbols indicate not only the elements but precise and accurately determined quantities. Thus the formula for water (H_2O) indicates not only that water is composed of the two elements, hydrogen and oxygen, but also that it results from the combination of one atom of oxygen with two atoms of hydrogen. As the atomic weight of hydrogen = 1, and that of oxygen = 16, it will be at once seen that eighteen parts of water consist of two parts of hydrogen and sixteen parts of oxygen. These figures apply equally to tons as to grams. The following is a similar calculation for phosphates; thus tribasic phosphate of lime contains :—

	Atomic Weight.
Calcium (Ca)	40
Phosphorus (P) =	31
Oxygen (O)	16

1. A molecule of $Ca_3(PO_4)_2$ therefore weighs :—

Ca_3	40×3	120
P_2	31×2	62
O =	16×8	128
		310

2. A molecule of sulphuric acid, H_2SO_4 ($H = 1$; $S = 32$; $O = 16$) $= 2 + 32 + (16 \times 4) = 98$. But tribasic phosphate of lime requires two molecules of sulphuric acid to render it soluble; we thus get $2 \times 98 = 196$ of sulphuric acid and $5 \times 18 = 90$ of water. Sulphuric acid may also be calculated as SO_3 and H_2O, or as anhydrous sulphuric acid and water. To render the phosphate soluble $5 + 2 = 7$ molecules of water are required. It follows, therefore, in order to dissolve 310 parts of tribasic phosphate of lime, that the 310 parts of $Ca_3(PO_4)_2$ must be put in contact with 160 parts of SO_3 and 126 parts of water. One part (say one ton) of $Ca_3P_2O_8$ requires therefore $\frac{160}{310} = 0{\cdot}516$ parts SO_3 and $\frac{126}{310} = 0{\cdot}406$ parts water, or for 100 parts :—

$$100 \times 0{\cdot}516 = 51{\cdot}6 \text{ parts } SO_3$$
$$100 \times 0{\cdot}406 = \underline{40{\cdot}6} \;\; ,, \;\; H_2O$$
$$92{\cdot}2 \text{ dil. } H_2SO_4$$

Now as 92·2 parts of H_2SO_4 contain 51·6 parts of SO_3, 100 parts contain $\frac{51·6 \times 100}{92·2} = 55·96$ SO_3. It is, therefore, acid containing 56 per cent of SO_3 that has to be used. On consulting the table by Lunge and Isler, at the end of this book, it will be found that acid of that strength has the specific gravity of 1·600 = 54° B. or 120° Twaddel. But in actual practice it happens that the acid used is more concentrated or more dilute. Suppose that the acid marked 60° B., according to the table above mentioned, containing 63·7 per cent SO_3, be used, it will be necessary to take $\frac{51·6 \times 100}{63·7} = 81$ parts to render 100 parts of tribasic phosphate of lime soluble, and it would be necessary to add the required amount of water thereto. If the acid weighs less than 54° B., say 50° B., the same method of calculation will give the quantity. Acid of 50° B. contains 51·04 per cent SO_3, therefore it would be necessary in such case to use $\frac{51·6 \times 100}{51·04} = 101$ parts for 100 of $Ca_3P_2O_8$.

Effect of the Impurities in Phosphates on their Behaviour in the Process by which they are Rendered Soluble.—Raw phosphates, however, contain several other compounds besides tribasic phosphate of lime—such as carbonate of lime, oxides of iron, and alumina, calcium fluoride, decomposable silicates, etc. If, therefore, the amount of sulphuric acid required for the phosphate only were taken, the latter would not be rendered completely soluble, because the sulphuric acid would act upon the carbonate of lime first and then the tricalcic phosphate. It is thus necessary to determine the percentage of these ingredients in the phosphate and allow for them in calculating the acid.

Carbonates of Lime and Magnesia.—In treating phosphates with sulphuric acid, the carbonates are attacked first. It is usually carbonate of lime that is present since carbonate of magnesia is only met with rarely, for example, in Carolina and Florida phosphates. Carbonate of lime is, therefore, dissolved at the very first, then follow the other compounds in the order of their relative stability. The decomposition of the carbonate of lime and the consequent formation of gypsum which follows causes an energetic reaction, which is very favourable to the progress of the decomposition. The heat disengaged is beneficial while the carbonic acid in its effort to escape raises the mixture, rendering it porous and spongy like a well-risen loaf in the baker's oven, and thus facilitates drying. More than 5 per cent of carbonate, however, acts unfavourably, in this sense that, leaving the expense of the extra acid out of account, it naturally results in an excessive amount of gypsum being formed, which is detrimental to the finished product, as will be seen in the

sequel. The quantity of acid absorbed by the carbonate of lime when in small amount (1 part of $CaCO_3$ requires 1·5 parts of SO_3) is compensated to a great extent by the advantages accruing in "mixing" and by the quality of the superphosphate. Phosphates free from carbonate of lime heat but little in contact with acid; the reaction is consequently slow, the operation takes longer and the final product is difficult to dry. To remedy this defect in treating phosphates of this nature—apatites, for example—it is best to mix them with phosphatic chalk during grinding, but the superphosphate which results is, however, not so homogeneous as that obtained from the chalky phosphates of Algeria. The amount of acid required to decompose the carbonates is calculated from the following equations:—

$$\underbrace{\underset{100}{CaCO_3} + \underset{98}{H_2SO_4} + \underset{18}{H_2O}}_{216} = \underbrace{\underset{172}{CaSO_42H_2O} + \underset{44}{CO_2}}_{216}$$

$$\underbrace{\underset{84}{MgCO_3} + \underset{98}{H_2SO_4} + \underset{108}{6H_2O}}_{290} = \underbrace{\underset{246}{MgSO_47H_2O} + \underset{44}{CO_2}}_{290}$$

Magnesia is also met with, but in smaller quantities, as tribasic or neutral phosphate. The following reaction then occurs:

$$Mg_3(PO_4)_2 + 2H_2SO_4 + 16H_2O = MgH_4(PO_4)_22H_2O + 2MgSO_47H_2O.$$
$$2MgHPO_4 + H_2SO_4 + 9H_2O = MgH_4(PO_4)_22H_2O + MgSO_47H_2O$$

Acid phosphate of magnesia is not deliquescent and not decomposed by water.

Iodine.—Certain phosphates contain iodine, as calcium iodide (CaI_2), which is converted by the sulphuric acid into hydriodic acid at the ordinary temperature of the "mixing"; when the mass heats the acid reacts on the hydriodic acid, forming iodine which is evolved as a violet vapour. Phosphoric acid has no action on hydriodic acid.

Calcium Fluoride.—Most phosphates contain more or less calcium fluoride. This substance is likewise decomposed by sulphuric acid at a temperature above 40° C. (104° F.). It is then given off as gaseous hydrofluoric acid. But the latter acts in its turn on silicic acid and forms with it silicic fluoride. These two reactions may be represented thus:—

$$CaF_2 + H_2SO_4 + 2H_2O = CaSO_42H_2O + 2HF$$
$$SiO_2 + 2CaF_2 + 2H_2SO_4 + 2H_2O = SiF_4 + 2CaSO_42H_2O$$

The silicic fluoride makes itself evident by a penetrating acrid odour; it decomposes in presence of water into gaseous hydrofluosilic acid which volatilizes, and orthosilicic acid

$$3SiF_4 + 4H_2O = 2H_2SiF_6 + Si(OH)_4$$

Gaseous Hydrofluoric acid acts on silicates to render them soluble :—

$$Al_2(SiO_3)_3 + 6HF = Al_2F_6 + 3H_2SiO_3$$
$$Al_2(SiO_3)_3 + 18HF = Al_2F_6 + 3SiF_4 + 9H_2O$$
$$CaSiO_3 + 2HF = CaF_2 + H_2SiO_3$$
$$CaSiO_3 + 6HF = CaF_2 + SiF_4 + 3H_2O$$

Ost observed that in the "dissolving" process two-thirds of the fluorine contained in the phosphates escapes as gas, whilst one-third remains as calcium fluoride; but according to Klippert 50 per cent of the fluorine is disengaged as gas, 30 per cent remaining undecomposed, and 20 per cent is absorbed mechanically by the mass as H_2SiF_6. Fossil bones may contain as much as 16 per cent of CaF_2.

Silicates of Lime and Alumina.—The silicates $CaSiO_3$, $Al_2(SiO_3)_3$ are partly soluble in sulphuric acid and partly insoluble. The silicates of lime in Algerian phosphate are decomposable by sulphuric acid, the silica being precipitated as a gelatinous swollen mass, which may enclose a certain amount of insoluble phosphate of lime protecting it from the action of the acid. The undecomposed silicates of alumina absorb acid mechanically and are gradually decomposed by it.

Oxides of Iron and Alumina.—The presence of oxides of iron and alumina in raw phosphates has serious drawbacks. It may in some cases prevent their use in superphosphate manufacture. The iron is present in different forms, most often as oxide combined as phosphate, more rarely as free oxide or as protoxide (ferrous oxide). It also occurs as sulphide, FeS_2, either in a fine state of division as in Tennessee phosphate, which contains as much as 4 per cent, in the river pebbles of the Carolinas, in certain Belgian phosphates, or as lamellæ in the phosphates of Podolia. But sulphide of iron is usually present in too small a quantity to cause serious trouble. Phosphates containing protoxide of iron (ferrous oxide, FeO) have a greyish-black or blueish-grey colour like certain Florida, Tennessee, and Carolina river pebbles. In the process of "dissolving" phosphates the iron compounds are decomposed more or less rapidly and completely according to the form in which they occur, according to the nature of the phosphates, the amount and the concentration of the acid used, and finally according to the extent to which the "mixing" becomes heated during the reaction.

Decomposition takes place thus :—

$$3FePO_4 + 3H_2SO_4 \leftrightarrows (FePO_4 2H_3PO_4) + Fe_2(SO_4)_3$$

If sulphuric acid be employed in excess all the phosphoric acid is liberated :—

$$2FePO_4 + 3H_2SO_4 \leftrightarrows 2H_3PO_4 + Fe_2(SO_4)_3$$

The decomposition of the phosphate of iron therefore yields phosphoric acid and sulphate of iron. A portion of this sulphate of iron reacts on the acid phosphate of lime with formation of a gelatinous precipitate, whilst a small proportion remains inactive and can be detected in the aqueous extract of the superphosphate. This amount is about 2 per cent. Consequently the presence of 2 per cent of oxide of iron in (raw) phosphate has practically no injurious effect, that amount remaining as soluble sulphate if the acid be slightly increased; when the proportion of oxide of iron amounts to 3 or 4 per cent it always causes a loss of soluble phosphoric acid. Beyond 4 per cent the phosphate becomes unfit for superphosphate manufacture. In his excellent treatise on superphosphates, Schucht insists on this special point and explains the precipitation of the phosphate of iron thus:

$$CaH_4(PO_4)_2H_2O + Fe_2(SO_4)_3 + 5H_2O = FePO_42H_2O + CaSO_42H_2O + 2H_2SO_4$$

$$H_2SO_4 + CaH_4(PO_4)_2H_2O + H_2O = CaSO_42H_2O + 2H_3PO_4$$

$$2(FePO_42H_2O) + 4H_3PO_4 = FePO_42H_3PO_4 + 4H_2O$$

He demonstrates the course of these reactions by the following small experiment. If to a solution of a superphosphate an acid solution of a salt of iron is added phosphate of iron is precipitated. But according to their degree of concentration superphosphate solutions act differently on solutions of oxide of iron; thus a 2 per cent solution precipitates immediately all the oxide of iron, a 4 per cent solution gives a weaker reaction, and in a 6 per cent solution the reaction occurs slowly. Consequently the greater the amount of free phosphoric acid in a superphosphate solution, the more it retains the iron in solution. If a solution of a ferruginous superphosphate be evaporated to dryness and water is added to the residue, a clear solution is not obtained, but a solution with a considerable precipitate. This hydrated phosphate of iron may pass in the superphosphate into the completely insoluble state, when its constitutional water is removed from it by the crystallization of the amorphous sulphate of lime:—

$$FePO_42H_2O + CaSO_4 = CaSO_42H_2O + FePO_4$$

This explains why an incompletely dissolved or retrograded superphosphate cannot be improved by further treatment with sulphuric acid. In such case there is obtained a wet tacky mass, the acid uniting with the gypsum to form $CaH_2(SO_4)_2$. It is only after a certain time, after numerous treatments followed by drying, that this free acid reacts on the non-decomposed phosphate, but not on the phosphate of iron. On the other hand, the hydrated phosphate of iron is soluble in the free phosphoric acid of the superphosphate, but only in a transitory fashion.

Oxide of alumina in the proportion in which it generally occurs as $AlPO_4$ in raw phosphates does not exert directly any influence on the retrogradation of the phosphoric acid. Contrary to what takes place with oxide of iron, the hydrated oxide of alumina $Al_2O_3 3H_2O$ does not become soluble in acid until after ignition. The hydrated phosphate of alumina as well as the anhydrous phosphate of alumina is soluble in the precipitated condition in phosphoric acid. That is why it is unnecessary to eliminate the phosphate of alumina from raw phosphate when it occurs only to a moderate extent. Alumina as silicate may prove injurious; if it be not decomposed by the sulphuric acid it may in certain cases cause the retrogradation of a portion of the phosphoric acid.

Organic Matter.—According to the origin of the phosphates organic matter may be present which is carbonized in the mixing process either by sulphuric or phosphoric acid. The dust given off by certain phosphates (Algeria, Gafsa) during grinding diffuses a bad odour which it is impossible to eliminate during manufacture. Ignition alone does away with it. Coprolites, Carolina phosphate pebbles, Algerian phosphate give off an odour of ichthyocol or o naphthene analogous to that given off on heating petroliferous shale, limestone, etc. These odours are due to the decomposition of the remains of the fat of marine animals. More often, however a penetrating odour is given off from phosphates, resulting from the evolution of volatile organic matter, which is not decomposed by sulphuric acid except at the high temperature incidental to the mixing process. These remains form a nitrogenized and sulphurous charcoal, which is then converted into compounds with an acrid and penetrating odour. Certain coprolities even exude a sort of tar during drying, equivalent to as much as 0·5 per cent of the mass. The above shows how variable the raw materials are which are met with in course of manufacture.

Method of Determining the Amount of Acid to use in Order to Render the Phosphate Soluble.—It was a long time before an agreement could be reached as to the quantity of sulphuric acid necessary to render the raw phosphate soluble. The manufacturer had the alternative of completely dissolving the phosphate by the use of a large quantity of sulphuric acid, but the superphosphate so produced was too moist to be spread by means of the drill, or of using less acid and only incompletely dissolving the phosphate. This difficulty has been overcome by installing superphosphate drying machines so that now there need be no difficulty in arriving at the requisite amount of acid to dissolve the phosphate completely. To calculate the acid some proceed in a purely empirical manner, by using 1 ton 4 cwt. of sulphuric acid of 50° B. for one ton of tribasic phosphate of lime, and adding the surplus of acid necessary to saturate the carbonate of lime; others saturate two atoms of calcium

with 550 grammes of sulphuric acid of 50° B. and increase this quantity by that necessary to saturate the carbonate of lime and the sesquioxide, three of sulphuric acid of 50 B. for one of sesquioxide; others, finally starting from the anaylsis of the raw phosphate, use the amount of acid necessary to saturate the sesquioxides and the total lime, less the portion of the latter inherent to the formation of acid phosphate of lime. The last method is evidently the best, since it is based on a well-accepted theory; it was always used for treating guanos, which, owing to the presence of bibasic phosphate of lime, were dissolved with the greatest ease. But as already mentioned, mineral phosphates often contain small amounts of silicates, which likewise absorb sulphuric acid. Taking the foregoing facts into consideration practical men have concluded that the best method is to make a trial mixing. These trials ought to be carried out each time on a sufficient amount of material to fill the mixer. Accordingly, the phosphate and acid are mixed by the aid of the agitator and the process is conducted exactly as in normal working. The reaction, which takes place in the mixing den, does not consist solely in the heating of the materials, as one would be inclined to imagine, because if that were the case the same result would be attained by heating the sulphuric acid or even the material on which it acts when working on the small scale. In the case of certain mineral phosphates, such as Canadian apatite, mixing test trials never succeed, because the phosphoric acid formed in the first phase of the operation cannot immediately exercise its action on the rest of the phosphate. The operation drags, the substance remains pasty, the sulphuric acid attracts moisture, its action gradually becomes weaker, and, finally, a bad quality superphosphate results. A rough trial test giving useful indications may be made when new phosphates of unknown behaviour are being bought in the slack season by treating the phosphate with acid in an earthenware bread pan, not stirring too much and setting aside with the pan lid on and inspecting the result after 24 hours' standing in a warm place. If the mixture dries, then it will dry far better on the large scale.

It is thus necessary when new phosphates are to be used, the behaviour of which during mixing is unknown, to make trial mixings with quantities of acid near to that obtained by calculation, and to adhere afterwards to the amount which gives the best results. With Florida phosphate good results are obtained by increasing the theoretical amount by 5 per cent. It is easy to understand, moreover, that the richer the raw material is in phosphoric acid the less it should be over-acidified, since the phosphates of that category generally contain little sesquioxides or silicates capable of absorbing the acid added in excess. Phosphates rich in carbonate of lime, such as Somme and Algerian phosphates, require more acid; but in any case the excess of acid rarely surpasses 5 per cent of the

quantity calculated according to their percentage of phosphoric acid.

If the trial mixing be well conducted it gives very satisfactory results. The superphosphate obtained should be comparatively dry and porous when it is cold. After each trial the phosphoric acid, soluble in water, the free phosphoric acid and the insoluble phosphoric acid are determined. Bone phosphates are almost completely rendered soluble. This, however, is not the case with mineral phosphates, which always leave a small amount of insoluble phosphoric acid. This fraction amounts to about 1·4 for Gafsa superphosphate, 1·7 for Algerian, 1·4 for Peace River and Pebbles, 0·5 to 1 for Florida, 1·7 for Carolina, and 2·1 for Tennessee (Schucht). Up to the present the efforts of scientists and practical men to abolish this loss have not been successful. The density and strength of the acid have considerable influence in mixing. Phosphates rich in carbonate work best with cold acid, whilst those poor in carbonate require hot acid. It has been found, moreover, that the soluble phosphoric acid is better preserved in superphosphates prepared with acid of 54° B. than in superphosphates made with acid of 50° B.

Damp phosphates and those difficult to dissolve require stronger acid than those which are dry and rich in carbonate of lime.

Finally, it is well to bear in mind that superphosphates should contain a certain amount of free phosphoric acid. This has the effect of retarding the neutralization of the acid phosphate of lime by the soil, and regarded from that point of view it constitutes an indispensable element of the superphosphate.

Schucht shows in the following table the amount and the strength of acid which it is convenient to use in rendering various phosphates soluble :—

TABLE XLI.—AMOUNT AND STRENGTH OF ACID REQUIRED TO DISSOLVE VARIOUS PHOSPHATES.

	$Ca_3P_2O_8$ Per cent.	Oxide of Iron and Alumina. Per cent.	Carbonate of Lime. Per cent.	100 lb. of Phosphate require lb. of Acid.	Degree Baume.[1]
Bone ash	82·1	0·3	4·4	95	52
Malden guano	72·4	0·3	12·5	82	60
Aruba phosphate	78·6	3·8	4·2	100	52·5
Curaçao phosphate	88·0	0·1	7·0	105	50
Podolia coprolites	74·7	5·0	4·7	120	50
Carolina phosphate	56·0	2·8	12·0	109	50
Canadian phosphate	76·8	3·3	6·6	110	55
Somme phosphate	67·0	3·8	10·2	105	51
Liége phosphate	55·5	3·6	16·8	105	50
Ciply phosphate	40·7	2·3	41·8	131	49
,, ,,	48·2	1·7	35·6	125	49
,, ,,	53·8	1·3	34·2	130	49
,, ,,	57·4	0·8	29·1	125	49
Florida phosphate	78·0	2·0	4·4	110	50
Pebble phosphate	68·0	1·8	6·3	100	50
Peace River phosphate	61·7	2·9	8·4	95	50
Tennessee phosphate	80·5	3·4	5·2	110	50
,, ,,	69·9	2·3	6·0	105	50
Algerian phosphate	58·2	0·5	20·8	110	50
,, ,,	65·0	0·6	16·0	100	52
Gafsa phosphate	59·6	1·7	9·7	100	50
Clipperton guano	78·7	0·1	6·7	100	52
Peruvian guano	26·2	0·5	1·8	25	60
Precipitated phosphate	32·0			55	60
Steamed bone dust	22·0	0·4	5·2	70	50
Degelatinized bone dust	31·0			74	55

Such a table is of course very valuable, but it is better to calculate all acid to B.O.V. whatever be the strength used. That keeps the acid account correct. But if the different strengths of acid used be all entered at the actual weight taken, then there can be no chemical control of the amount of acid used; nor if the manure manufacturer makes his own acid of the amount of acid he has made. The general rule is to take the stock of acid in hand, calculate it to B.O.V., add to it the amount used in mixing, and take that as the amount of acid made in the season, which, checked against the pyrites burnt, say Rio Tinto, should give a yield of 30 cwt. B.O.V per ton of pyrites burnt.

[1] (1) 49° B. = D 1·515 = 103 Tw. (2) 50° B. = D 1·530 = 106 Tw. (3) 51° B. = D 1·546 = 109·2° Tw. (4) 52° B. = D 1·563 = 112·6 Tw. (5) 52·5° B. = D 1·572 = 114·4° Tw. (6) 55° B. = D 1·615 = 123° Tw. (7) 60° B. = D 1·710 = 142° Tw. (8) Acid in Great Britain is generally used as near D 1·60 = 120° Tw. as practicable. B.O.V is acid of D = 1·700 or 140° Tw.—Tr.

CHAPTER VI.

MANUFACTURE OF SUPERPHOSPHATE.

THE manufacture of superphosphate comprises three principal operations: 1. Grinding the raw phosphate. 2. Rendering the ground raw phosphate soluble by sulphuric acid. 3. The drying of superphosphate.

Grinding Raw Phosphate.—Raw phosphate should be carefully ground, because it is found that the fineness of the phosphate contributes to a great extent to the successful preparation of superphosphate. Thus the powder should not leave more than 10 per cent of residue on a 70 mesh sieve, and this residue should not exceed the size of groats; it is only when this is done that all the phosphoric acid is rendered soluble. Certain phosphates are delivered ground, others in lumps of the size of the fist. To lend itself well to grinding the phosphate should be *dry*. Florida phosphate especially should not contain more than 1 per cent of moisture, whilst Algerian phosphate grinds very well with 5 per cent of water. When dealing with phosphate drenched with sea water in transit or accidentally in the warehouse, it is spread upon a drying platform of sheet iron heated by the waste gases from the flues from the boiler furnaces. In the grinding of phosphate at the present day ball-mills—continuously feeding and discharging—are in general use, which, owing to their strong construction and their steady output answer well for the purpose. In older factories flatstone mills are frequently used. Griffin's crusher with walking beam is likewise used in some rare instances, but it is costly and requires frequent repairs which become heavy as time goes on. The material to be introduced into this grinding machine ought preferably to be reduced in size, and for that purpose edge runners are suitable. The crusher, with blades—disintegrator—is likewise used, but only to crush phosphate in the form of large nodules or rock phosphate. These machines will now be briefly described, along with the other grinding machines commonly used in the manufacture of chemical manures.

Grinding Machines—Edge Runners.—Edge runners consist usually of two stones running on a circular plate which revolves round a vertical shaft; at the same time each stone turns round its

own horizontal axis, and grinds the material both by crushing and rubbing. The horizontal axes of the two mills are independent of one another, each being connected with the vertical shaft by means of a hinged crank. The stones can thus be raised or lowered independently of one another. The material is fed into the mill directly, by the shovel or by an elevator; it is drawn continually under the stones by scrapers, and when it is sufficiently ground, it is evacuated by the automatic discharge, sifted and bagged up. Fig. 1 shows a

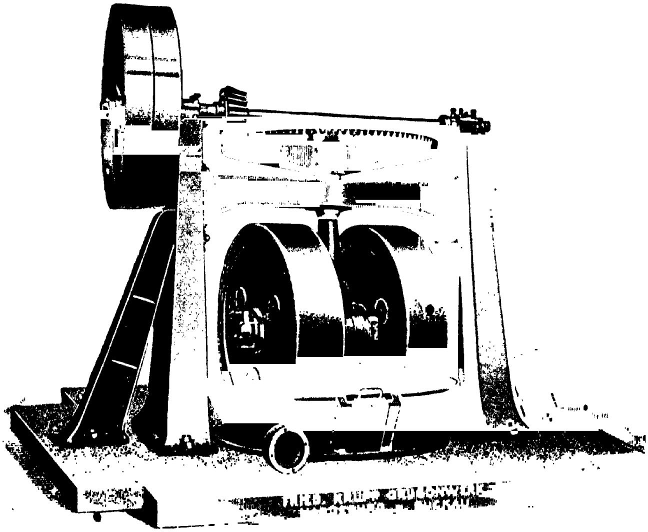

FIG. 1.—Vertical Edge Runner.

pair of edge runners. Two men suffice to attend to the mill, the elevator, and the sifting machinery.

Flatstone Mills.—In flatstone mills there are two stones, one which is caused to revolve, the other being stationary. The upper or lower stone may be stationary, whichever may be most convenient. Mills of the first kind are used for crushing very hard phosphate, those of the second kind for soft phosphates. The foundation consists of cast-iron columns or a hollow cast-iron support, on which the cage of the mill is fixed. The shaft of the mill is sustained by a movable bearing with collar; its lower part rests in a socket. The bearing with collar is screwed to the bottom of the mill cage and

is completely protected from dust. The adjustment of the revolving millstone is done by means of an endless screw or by lever transmission with screw, and hand fly-wheel. The number of revolutions is 120 per minute for mills 5 feet in diameter, under which conditions a mill can grind about 5 tons of phosphate per hour, with 20 H.P. The mill is fed by a cup elevator and a shaking hopper, a single

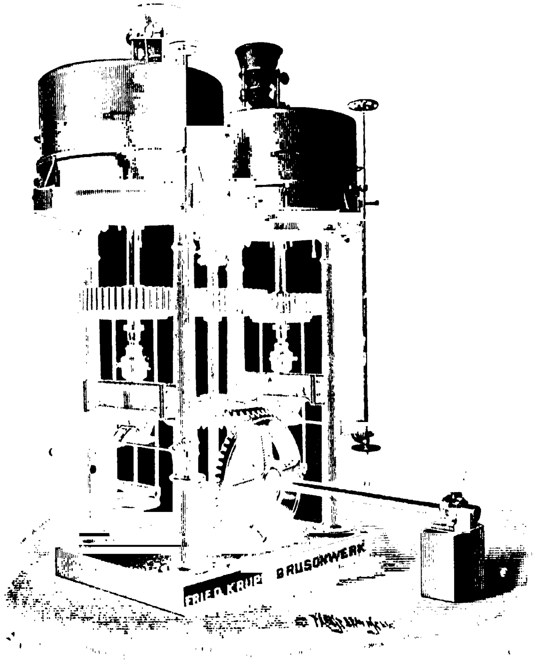

FIG. 2.—Flatstone Mill. (Lower stone dormant.)

workman with an assistant being able to attend to two pairs of stones placed side by side. The mills of each group are generally driven by a single main shaft by direct cog-wheel gearing. Generally three pairs of stones are in each group, two of which are at work and the other pair being refaced. Fig. 2 shows two mills with the lower stones stationary arranged in a group driven from a common shaft by conical gearing.

Ball Mills.—The ball mill consists essentially of a rotary drum

enclosed in a double cast-iron envelope and sieves. It contains a number of balls of different sizes. The inside face of the bottom of the drum is lined with smooth plates of hardened cast-iron or of cast-steel. The circumference consists of triturating plates of cast-steel, and of such a shape that a fall is created between each two consecutive pieces. It follows that during revolution the balls fall from one plate to the other, and roll during the interval between

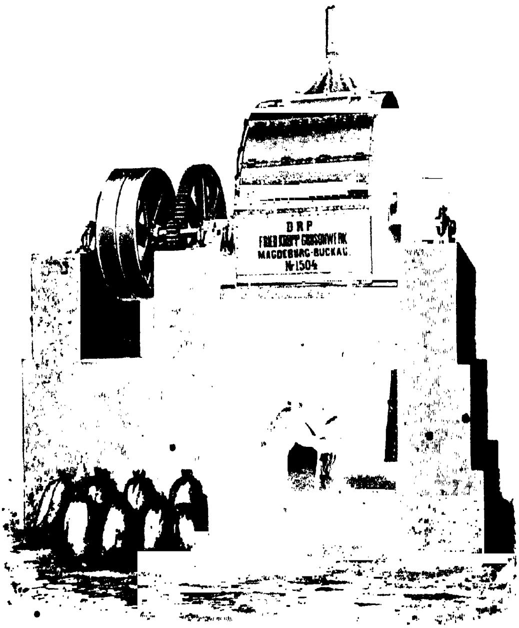

FIG. 3.—Ball Mill on Masonry Foundation.

two falls. Grinding is thus effected by the shock of the falling balls and by crushing. The substance ground in the ball mills passes through holes in the triturating plates and falls on a first sieve, called the protection sieve, which retains insufficiently ground fragments of material, allowing only particles of a certain fineness to pass through. The fine grains then fall on a second sieve, the outside sieve, the wire gauze of which is selected according to the degree of fineness desired. The finely divided powder which passes

through this gauze falls into the discharging funnel at the bottom of the machine, and thence into the bags. The residues from the two sieves are collected inside the mill by two openings arranged for the purpose, and are again submitted to the action of the balls. The mill is fed through a hopper fitted over one of the bosses, which has helicoid blades. During rotation of the mill these bring the lumps into the interior after the style of an endless screw. The wrought-iron cover is connected by a cloth sleeve with a chimney

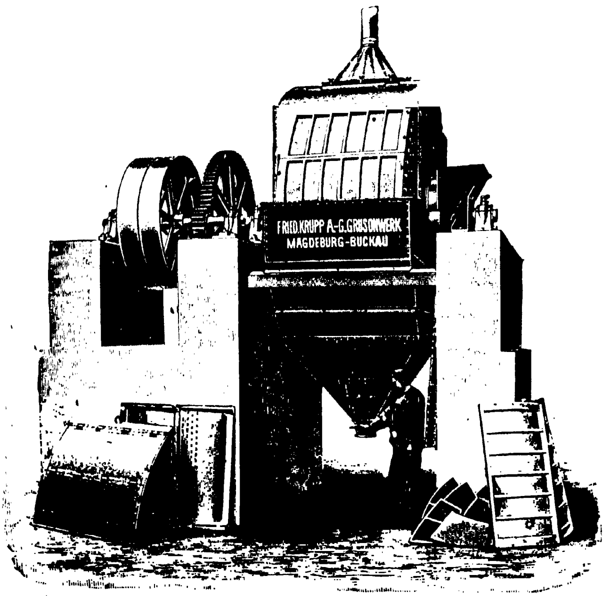

FIG. 4.—Ball Mill on Masonry Foundation—the Sieves exposed.

which maintains the pressure of the air in the cover in equilibrium and evacuates the dust which is given off during grinding. The weight of the balls varies according to the nature and quality of the material to be ground. The mills in general use have a diameter of 6½ feet and a width of 39·3 inches. The charge of balls weighs 1 metric ton. These naturally undergo a certain amount of wear. It has been found that in grinding Florida phosphate forged steel balls lost 1 kg. (2·2 lb.) in a year, working day and night, whilst cast-iron balls lost 420 grms. (nearly 1 lb.) in twenty-four hours. Their

weight must thus be verified from time to time. To start the mill it is revolved empty for half an hour to see whether there is any heating in the bearings. Then only is it charged with balls and phosphates. The drum ought always to be sufficiently full of material that the falling balls produce a dull or deadened sound. Consequently, as soon as a bag of ground material is taken from the mill, another is fed through the hopper. When there is not sufficient

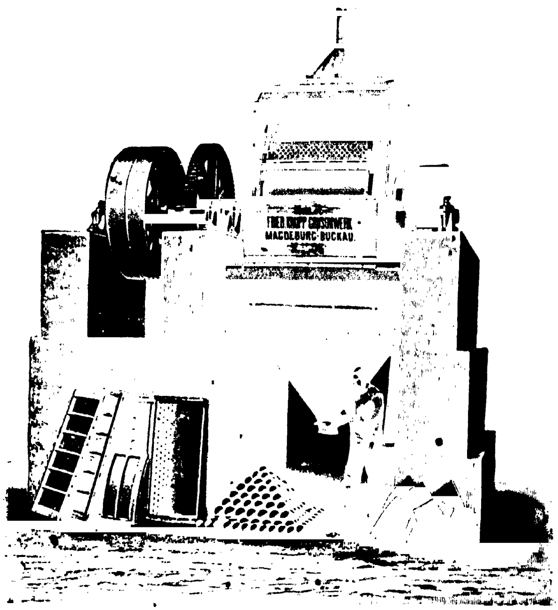

FIG. 5.—Ball Mill on Masonry Foundation—the Trituration Plates exposed.

feed on the mill its output is small and the workman is tempted to increase the load of balls, which has many drawbacks. The outer sieves are mounted on marked oak-frames, which prevent their being inverted, for they are not interchangeable. To stop up gaps or tears the simplest way is to glue pieces of calico over them with fish glue. During stoppages the inside of the drum is carefully inspected, the nuts of the frames and those of the manhole doors tightened, because, in spite of the use of double nuts, they are liable to work loose under the vibration to which they are exposed. Care must be taken to

keep the sieves in perfect condition. If the output of the mill

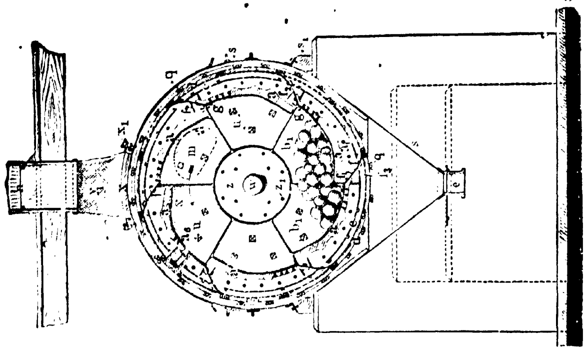

FIG. 7.—Ball Mill (cross section).

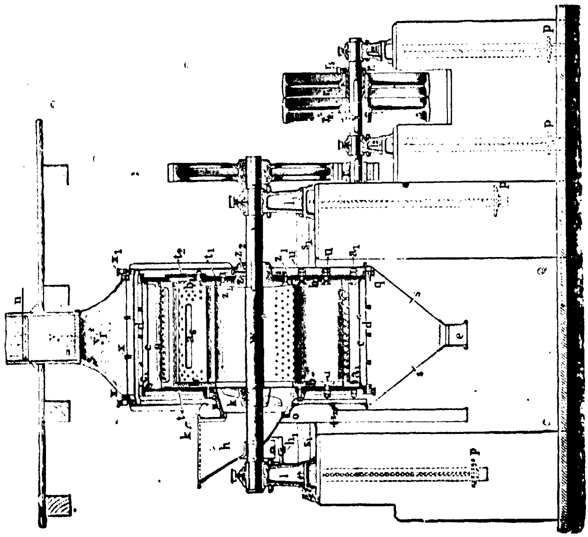

FIG. 6.—Ball Mill (longitudinal section).

decreases, both of the sieves must be speedily cleaned. For that purpose the double envelope must be removed by a chain and

counterpoise. In grinding wet phosphate the sieves soon become choked and they need to be replaced by new at short intervals. It suffices in order that the phosphates may be rendered soluble that they pass through Nos. 60 to 80 mesh sieves, according to their origin and their nature. Thus Algerian phosphates and Carolina phosphates are passed through a No. 60, whilst coprolites, apatites, and Florida phosphates must pass through a 70 mesh sieve. Guanos and bone phosphates do not require to be ground so fine, since, owing to their porosity, the sulphuric acid penetrates easily into the interior of the granules. It suffices to pass them through a No. 50.

List of the separate pieces forming Krupp's Ball Mill (see Figs. 6 and 7).

a	Triturating perforated plates.	n	Damper.
a^1	Collar screws.	p	Anchor plates.
a^5	Chimney plate.	r	Cog wheel.
a^6	Chimney cover.	r^1	Pinion.
b	Lateral plates (feed side).	r^2	Fixed pulley.
b^1	Lateral plates (rear side).	r^3	Loose pulley.
u	Screws of lateral plates.	r^4	Case for same.
c	Coarse screen.	r^5	Lubricator.
c^1	Screw of same.	s	Dust cage.
d	Fine sieves (frame and cloth).	s^1	Wooden supports.
q	Screws of sieve frame.	s^2	Collecting hopper and pipe.
e	Discharging funnel of dust cage.	t	Anterior lateral side.
f	Revolving blades.	t^1	Lateral posterior side with man-hole in.
f^1	Blade screws.	t^2	Manhole lid.
f^2	Protection Screens.	v	Cog wheel shaft.
f^3	Support of coarse screen.	w	Main shaft.
g	Opening for the return of material.	x	Frame work of dust cage.
h	Feed hopper.	x^1	Corner of the frame work.
h^1	Screw of hopper leg.	y	Aeration chimney.
k	Feed and boss.	y^1	Coarse cloth union.
k^1	Screw of feed boss.	z	Rear boss.
l	Column supporting hopper.	z^1	Screw of boss.
l^1	Rear column.	z^2	Fixing screw.
l^2	Gearing columns.		

As already mentioned, the ball mill is surmounted by a chimney. This ends in a dust chamber on the floor above; this chamber is itself provided with a ventilating pipe on the side opposite to that of the mill. When the chamber is not sufficiently well ventilated, the steam passing from the ground material condenses, the dust becomes wet, and the wood rots. It is, therefore, well to cover the sides with a coat of tar. In front of the chamber, that is to say at the point where the dust collects, are fixed two pipes closed by dampers, through which the dust falls into the grinding-room. It is, likewise, advisable to fix a fan to the dust chamber, so as to renew the air in the grinding-room. A greater quantity of dust

in this case collects in the chamber, which then requires more frequent cleaning out. A fan with a speed of 200 revolutions suffices for two mills. A ball-mill $6\frac{1}{2}$ ft. dia. requires 20 H.P.; it will grind $7\frac{1}{2}$ tons of Florida phosphate, so as to pass through a 70 mesh sieve in twenty-four hours. It works continuously, and yields in a single operation a sifted and ground substance without other preparation than the previous "cracking" of the phosphate so as to reduce it to lumps the size of the fist.

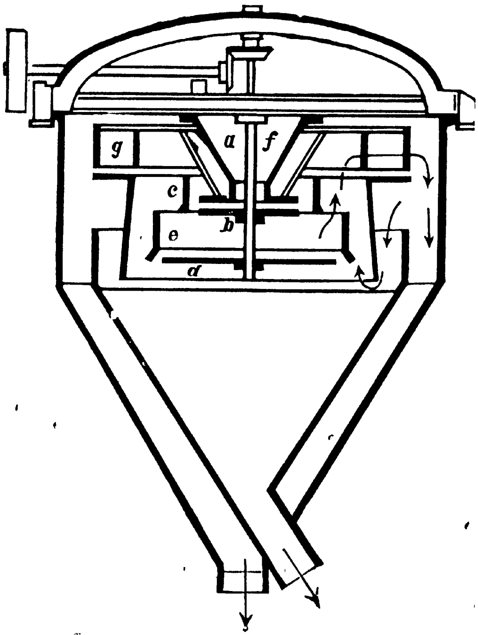

FIG. 8.—Pfeiffer Separator.

In certain cases, especially in grinding basic slag, particles of iron may remain in the mill, which cannot be ground. They are removed through an opening made in the side which in normal work is closed by a lid which can be replaced by a discharge grating. The distance between the bars of this grating being inferior to the normal diameter of the balls, it suffices to give a few turns to the mill to evacuate the residual matter. In large-sized mills a man-

hole, fixed in one of the cheeks, enables the interior to be inspected. Ball mills have been the subject of many improvements. Those made by the firm of F. Krupp, Grussonwerk Magdeburg, are of such solid construction as to stand any test and work for years without any repairs. The construction of this machine requires, in fact, a powerful equipment and select materials, conditions to which sixth-rate constructors can make no pretension.

Pfeiffer's Mill with Combined Air Separator.—This ball mill is most interesting owing to its originality and its great working capacity. But its yield is perforce limited by the simultaneous sifting of the ground material; it gradually diminishes the fineness of the sieves, the area of which is, moreover, too small compared with

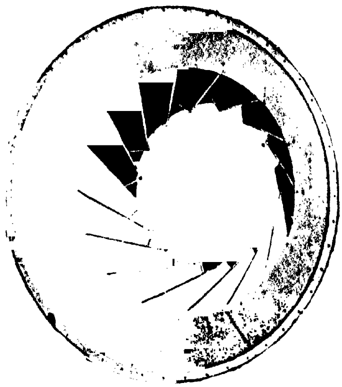

FIG. 9.—Pfeiffer's Separation Cone.

the work capable of being done by the mill. Moreover, if the mill be overfed, the substance treated penetrates into the cavities of the sieve before being reduced to the desired fineness; the sifting being then retarded as well as the normal work of grinding. But affairs are radically altered if the powder be sifted separately. There is then no obstacle to an increased production by this machine. This improvement has been effected by the firm of Pfeiffer Brothers of Kaiserlautern. By combining the ball mill with an air separator they have succeeded in creating a system of grinding remarkable for its great simplicity and in increasing considerably the useful effect and output of the mills. The construction of the machine differs from that of the ball mill in the following details. The grinding-stages are comparatively small, each consists of a single piece of crucible cast-steel made with particular care, they have no slopes nor orifices

of any kind to weaken them. Consequently they maintain their mechanical resistance to the last stage of wear and tear. There is no fear with this machine of the balls plugging the escape orifices, besides there is no need to enlarge these orifices by a rimer. The excel-

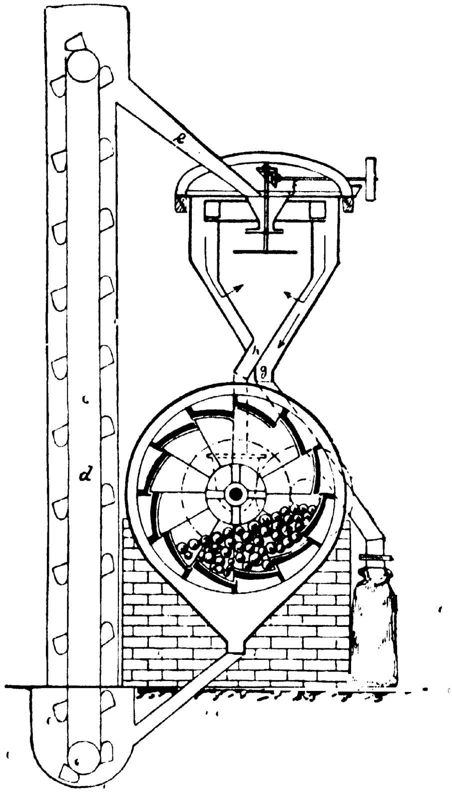

Fig. 10.—Section of Pfeiffer's Crusher-Separator.

lent construction of the triturating plates and the quality of the metal used render them almost everlasting. The plates from one stage to another are fitted with orifices which allow the sufficiently ground material to escape. These orifices can be regulated from the out-

side, and they may be contracted or enlarged as required so as to reduce the material to the required degree of fineness. As in ordinary ball mills, the wrought-iron cover which surrounds the drum ends in its lower part in a hopper; this collects the ground material and leads it to a cup elevator, which conveys it to an air separator, generally placed above the mill. In this air separator, the fine flour is separated from the grains by mean of a cyclone of air produced in the machine itself and circulating there. The

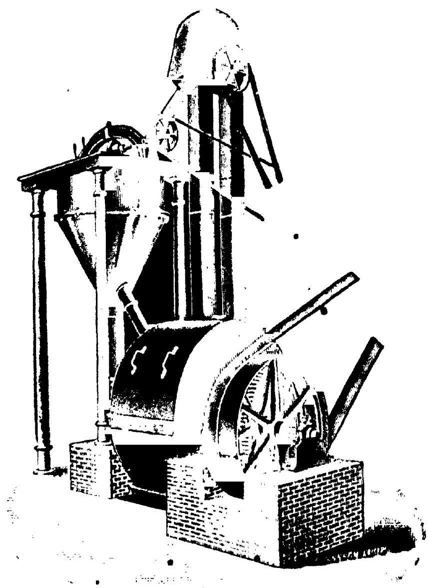

FIG. 11.—Perspective view of Pfeiffer's Crusher-Separator.

machine has only three orifices, the feed entrance, the exits for the granular material, and for the flour. It requires neither sieve, dust chamber, nor auxiliary apparatus of any kind. The separator is shown in section in Figs. 8 and 10. The machine is constructed of wrought-steel, and consists of a cylindrical envelope with exterior cone and an interior cone arranged at a certain distance from each other. The ventilator *g* is driven by the shaft *f*. On the same shaft, below the ventilator, are two plates *b* and *d*, which receive the material from the feed funnel *a*. In consequence of the rotation,

the distributors y project the substance in all directions, and the current of air produced by the ventilator passes from below, upwards. The force of the current raises the fine particles, and carries them in its train through the ventilator, and projects them against the exterior side, whence they fall into the *exterior* cone and issue from the central aperture. The larger granules contained in the material which have traversed the current of air, without being carried away in its train, fall into the *interior* cone and issue by the lateral pipe, to repass into the mill if necessary. The air returns naturally to the space below the distributor, so that the separator works constantly with the same amount of air, and there is no disengagement of dust. The rods, with pins, to be seen on the

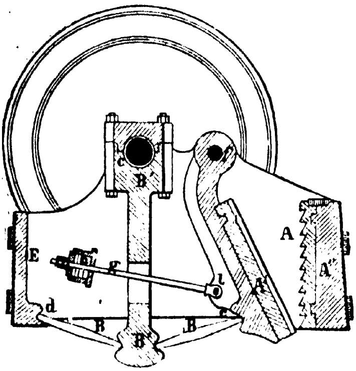

FIG. 12.—Jaw-breaker Crusher.

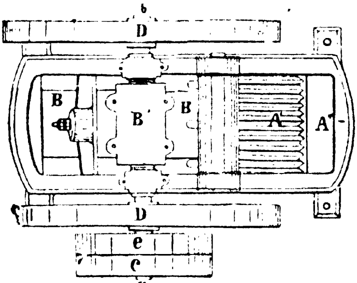

FIG. 13.—Jaw-breaker Mill (view from above).

cover of the separator, serve to raise or lower the annular obturator which regulates the degree of fineness of the substance. The force of the current of air diminishes in proportion as the obturator is raised. By these simple means, any degree of fineness can be secured. Once regulated, it works without interruption and supervision, and always gives a very uniform product. The ground phosphate can be bagged up directly or conveyed to silos, etc., whilst the granular portion returns to the mill to be further ground.

Jaw-breaker Mills, Cracking Mills.—The jaw-breaker mill shown in Figs. 12 and 13 consists essentially of two jaws, A′ and A″, of hardened cast-iron, ridged or smooth. One of these jaws, A″, is fixed on the anterior side of the framework, the other, A′, is mobile and fixed on a jaw-holder which is animated by a to and fro motion round its axis f. This motion is transmitted by the excentric

driving shaft c, through the intermediary of the excentric crank B′ and of a folding lever, formed by two hinge plates, BB, applied

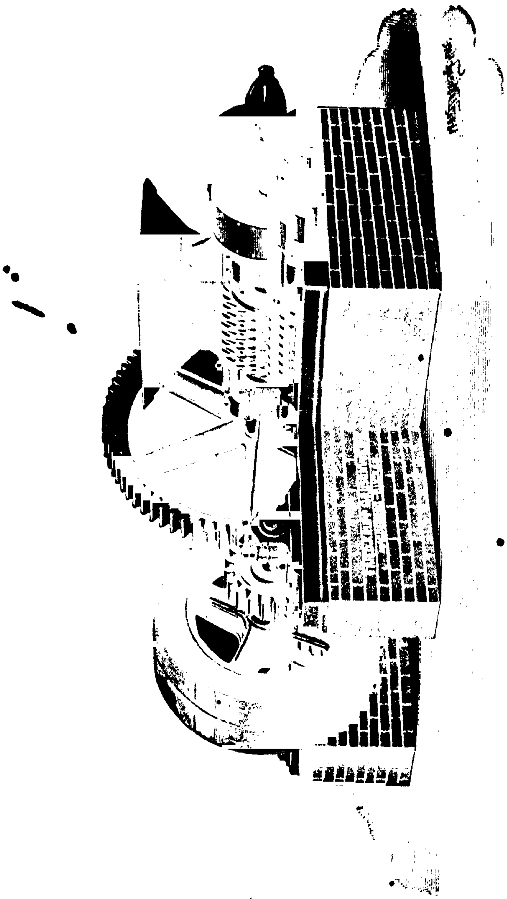

FIG. 14.—Toothed Roller Mill (belt driven).

one on the framework in d and the other on e on the lower part of the movable jaw-holder. To avoid shocks the latter is joined

in an elastic manner with the crank B, by means of the spring g. For each revolution of the shaft c the space A comprised between the fixed jaw-blade and the movable jaw is contracted, and its minimum aperture determines the size of the crushed pieces. The angle of the aperture of the jaws is easily adjusted by a very simple regulating arrangement, according to the nature of the material to be ground, and the degree of fineness required. The size of the

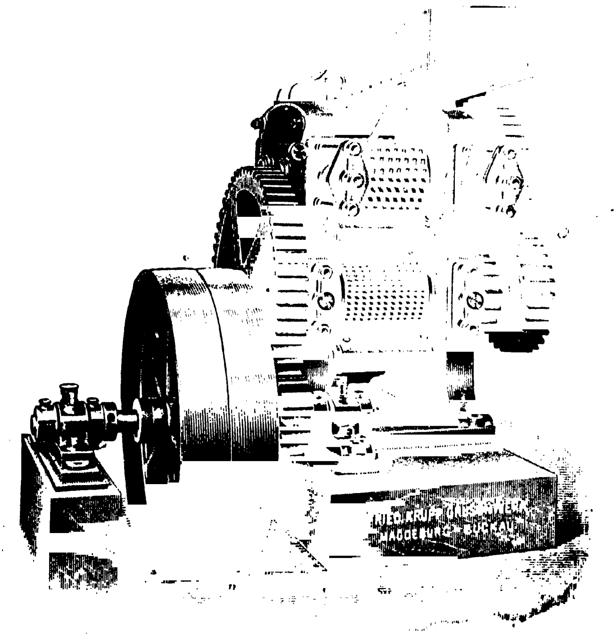

FIG. 15.—Double Roller Mill.

pieces may vary from 2 to 7 cm. in section, with a proportion of core, which depends on the degree of friability of the material. The hinged plates BB constitute a safety device; they avoid any sudden shock, such as would be caused by the passage of a hard substance, a piece of iron, for example, and then yield without any of the essential part of the machine being damaged. This mill is used for the preliminary crushing of rock phosphate, or phosphate in nodules of a certain size. It is fitted with two very powerful fly-

wheels, which ensure regularity in working. A crusher of this sort, with a speed of 200 revolutions a minute, can crush 5 tons of phosphate an hour with 3 H.P. Hand cracking, formerly in vogue, is now only adopted occasionally, when the quantity of

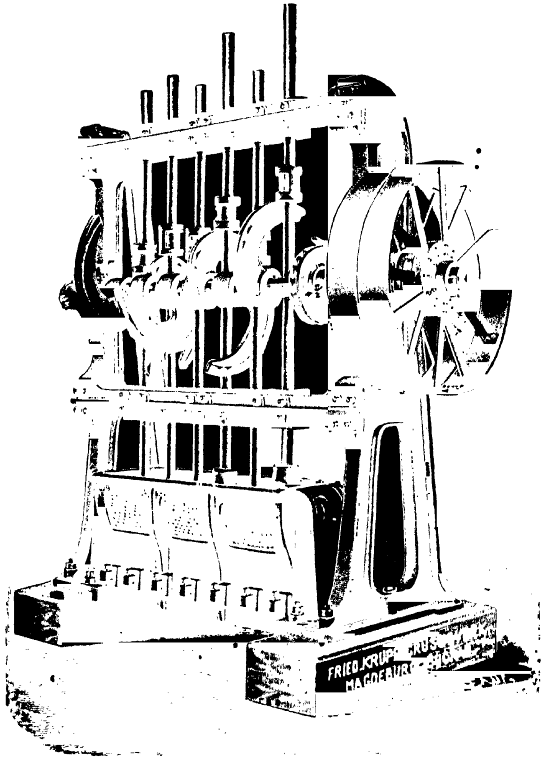

FIG. 16.—Stamping Mill.

phosphate in the form of large lumps is not enough to warrant the use of the engine.

Toothed Roller Mills.—To crush green (raw) bones for fat extraction simple and double mills are used with toothed steel rollers. The rollers of the simple mill consist of a number of steel discs fitted

with teeth, and of alternate rings in juxtaposition, in such a manner that the teeth of one of the rollers corresponds to the rings of the other. The discs resist great pressure and are readily replaced. The distance between the rollers can be regulated according to the size of the grain desired, by means of a regulating screw fitted with a spring stud. This machine reduces the bones to the size of a nut, mixed with granules, which are separated by sifting. The double mill comprises two pairs of rollers in a strong lateral framework. The upper pair is provided with large teeth and revolves at a slower speed

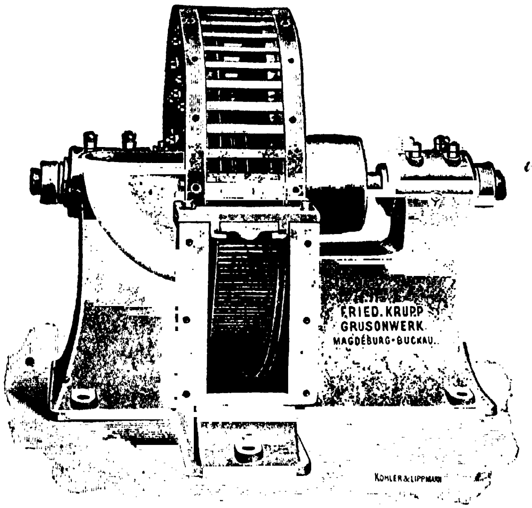

FIG. 17.—Disintegrator with outer casing removed.

than the lower pair, the teeth of which are finer. These double mills are capable of taking bigger bones (whole ox or horse skulls) than the simple mills. They also grind finer, which is an advantage in making gelatine, when it is desired to extract as completely as possible and to obtain gelatine of good quality. The output of these machines is about 1½ tons of crushed bones per hour.

To grind degreased bones cast-iron stamping mills, fitted with a steel grid in the bottom, and on the longitudinal side with wrought-iron sieves, are used. The fineness of the holes in the grating and the meshes of the wrought-iron sieves depends upon the size of

grain desired. Stamping mills contain 1, 2, 3, 4, 6, 8 or 10 stamps weighing 1 to 2 cwt. each; their yield per hour is about ½ ton of ½ inch bones.

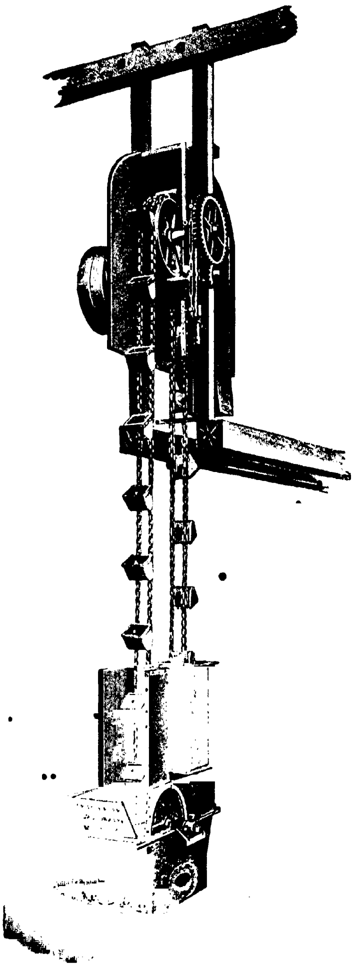

FIG. 18.—Cup-chain Elevator.

Disintegrators—Mills with Percussion Blades Fitted in Circular Revolving Boss.—For grinding raw bones, dried meat, and blood, disintegrators are used with advantage. The mill consists essentially of a framework with vertical grinding cage, in which a boss fitted with blades revolves at high speed. The cage consists of two lateral sides with a cover of wrought-iron, and a semicylindrical grid in two pieces, or completely cylindrical in four pieces. The lateral sides are lined inside with grooved plates of hardened cast-iron. According to the size of the mill the material to be ground may be in fragments of the size of an egg to that of the fist. When it is fed through the hopper it is struck by the revolving blades and projected against the grooved plates and the steel bars; it thus undergoes very energetic grinding; when it is reduced to the desired fineness it passes through the bars of the grid as a pulverulent product containing more or less core. For a width of ⅛ of an inch the yield per hour is stated to be about 2 tons

of degreased bones, but this result appears too high for such fine grinding. (See pp. 120 *et seq.*)

Elevators.—Cup elevators are generally used. Gall's wrought-iron chain and Ewart's chain deserve notice. These consist of small elements moving one within the other after the style of a hinge. Leather belts and rubber belts are only used exceptionally. The cups are of wrought-iron furnished in the front with steel armatures; they are screwed on the chains of the elevator. Their dimensions vary with the size of the factory. Cup chains are generally fitted with a tight cover, enclosing the whole machine, thus preventing the disengagement of dust in the factory. This cover comprises a cast-iron feed vessel with the top part of wrought-iron, and two square wrought-iron pipes carrying at their upper

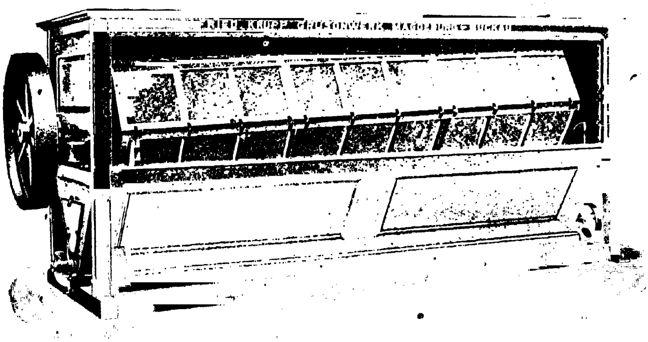

FIG. 19.—Sifting Machine (driven direct, enclosed in wood cover).

extremity a hood or coping of wrought-iron, fitted with a discharge pipe; wooden feed vessels and covers may be made on the spot.

Sieves.—The sieves used in the chemical manure trade are of two kinds, viz. sorting sieves and sieves for fine flour. The sorting sieves are combined with the coarse crushers serving to sort the crushed material; the portion which passes through the sieve is taken to the mills to be reduced to a fine powder, whilst the core is returned to the crusher to be further reduced. Machines of this nature are conical or cylindrical. They consist essentially of an axis, which passes through their entire length, and carries iron stays, on which a perforated sheet-iron sieve, more rarely a metallic wire gauze sieve, is mounted, the meshes of which have a section varying with the nature of the material to be ground. They are fitted with a feed hopper and a discharge pipe.

The second class of sieves are more especially used for the

sifting of the flour produced by the mills. They are also used to sort bone dust. The matter which passes through the sieve is bagged up, whilst the core passes out at the end and is returned to the mills to be reduced to the desired fineness. As the material gives off much dust the sieve is generally covered in. Discharge pipes pass through the bottom of the cover. The construction of the machine varies according to the nature of the material treated—with substances easily sifted, the cylindrical form is used, whilst with substances which pass through with difficulty, a hexagonal sieve fitted with a beater is used; the frames of the sieve are interchangeable and easy of access. Fig. 19 shows a sifting machine, driven direct, with wooden cover. Besides these cylindrical sifters, shaking sieves are also used, comprising one or more flat sieves lodged inside a cover. The cover rests on springs and is suspended and agitated by a crank shaft.

Filter Press.—The filter press is capable of interesting applications, not only in the manufacture of double superphosphates and precipitated phosphates, but also in the treatment of raw phosphates, with a view to their enrichment each time that they have to be washed or mixed.

After mixing, the materials have a semi-fluid, non-pasty consistency. It is, therefore, necessary to separate the solids from the liquid mass in which they are suspended. The old decantation process gave good results. But the enormous quantities now treated daily renders it an extremely slow process requiring numerous vessels and considerable space. In well-organised factories at the present day, a rapid method of decanting answers an urgent want. This rapid decanter is nothing more or less than the filter press, the yield from which is twenty times greater than that of the old process.

Under a small compass the filter press is, therefore, an apparatus presenting such a filtering surface that the solids and liquids are automatically and instantaneously separated. This apparatus consists essentially of a number of wood or metal plates separated by hollow frames, in which the solid matter aggregates as more or less compact cakes, whilst the liquid is pressed out, passing through appropriate filter cloths.

The filter press is fed by a pump which propels the mud into the filtering chambers. The chambers are made tight by the pressure system of the filter and by the packing which the filter cloths give between the different plates when the latter are forced together by the central screw. As regards the filtration of phosphatic material, manures, etc., the filter presses ought to exhibit such peculiarities of construction as to ensure the flow from the material without the formation of channels during the course of the operation. On the other hand, when the cakes are formed in the frames of the

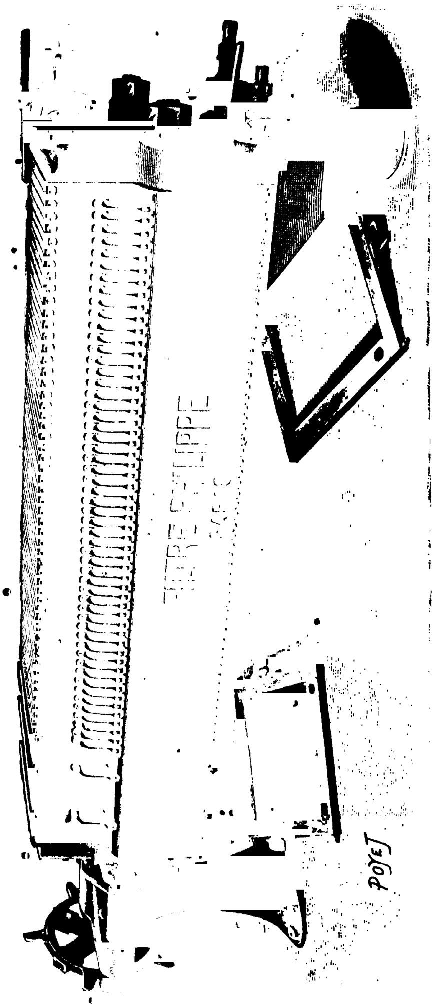

Fig. 20.—Filter Press.

filter presses they still contain a certain amount of mother liquor. To obtain products as pure as possible these cakes must be washed thoroughly to remove from them the liquids which they contain. The filters should be so arranged that this operation of washing is thoroughly and absolutely effective.

Mixing of the Phosphate with Sulphuric Acid.—As already mentioned, the phosphate was formerly rendered soluble in pits, in which the acid and phosphate were hand-mixed with suitable tools. In other words, they worked like masons making mortar. But for thirty years this work has been done exclusively by mechanical means, which enables the mixing to be done more rapidly and in larger quantities at a time.

Consequently the mixing pit has been enlarged so much that in its new form it constitutes the chamber, or more familiarly the "den" or "house" in which the phosphate is rendered soluble. This chamber is closed, and care has to be taken to eliminate and render inoffensive the toxic gases which are disengaged from the material during its decomposition.

To mix the acid with the phosphate a "mixer" or mixing machine is used, constructed and installed thus: The mixer consists of an egg-shaped pan 1·6 metre (about 64 in.) wide at the top and 1·20 metre (48 in.) wide at bottom, fitted with two discharge doors, with lever and counterpoise, which enables the mixing to be run into an enclosed space, called the decomposition chamber ("den" or "house"), built on the ground floor or sunk in the ground. The pan is fitted with a vertical shaft, driven by cog-wheel gearing, and carrying blades of a special form arranged in a helicoid manner; these lift, throw down, and triturate the mass, after the style of a plough as it works the ground, preventing it at the same time being deposited on the bottom and attached to the sides. It suffices to pull the levers to open the discharge doors, and thus let the liquid *a purée* fall into the decomposition chamber ("den" or "house").

The work is easy and rapid. The pan is made of cast-iron, with 2 per cent of a special alloy which renders it very resistant to acid. The arms of the agitator and the blades as well as the valves are of cast-steel. The mixing shaft makes sixty revolutions a minute; the mixing is triturated (churned) until the pulverized phosphate is intimately incorporated with the acid. When the ground phosphate is too coarse to pass through a 70 mesh sieve the mixture remains longer in the liquid state, in which case the length of time occupied in mixing must be prolonged. The acid, contained in a lead-lined tank, is run into a measuring tank by opening a valve; it flows through $1\frac{3}{8}$ inch lead pipe into the mixer in the form of a shower like rain. At the same time the crushed phosphate—previously weighed and laid on sacks on two inclined planes to right and to

left of the mixer—is run into the mixer. In certain factories the phosphate is brought to the mixer by an elevator, and received in buckets by means of which it is run into the mixer. The bags retain

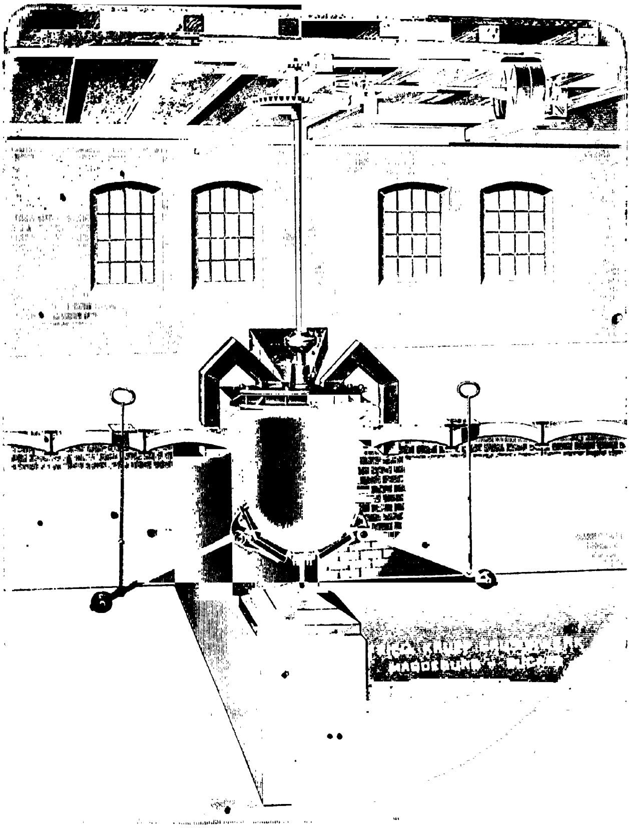

FIG. 21.—Mixer installed above the Superphosphate "Den".

about 1 per cent of phosphate in the fabric. The mixer can accommodate a charge of 225 to 250 kg. (495 to 550 lb.). When the phosphate is rich in carbonate of lime the mixture froths and

threatens to prime. Such a mishap is obviated by diminishing the flow of phosphate. The acid and phosphate should be run in simultaneously and not one after the other. The mixer works continuously; no stop is made except in case of a breakdown. When one "mixing" is finished and discharged the sides of the mixer are rapidly dusted with a little phosphate to neutralize any free acid left there which might corrode the metal. The working of the mixer requires the service of three men; the first takes charge of the machine, the second superintends the measuring and running in of the acid, the third brings the sacks of phosphate. The charging of the mixer occupies 1½ minutes; agitation requires two

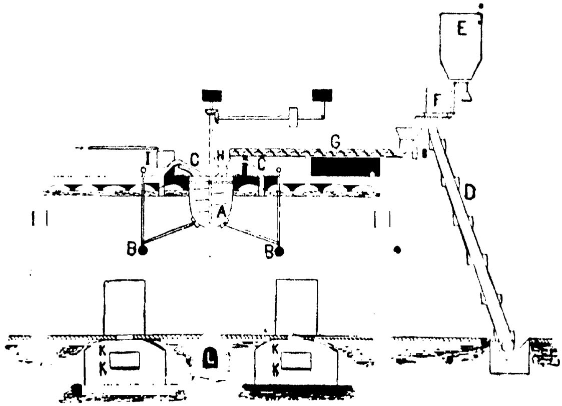

FIG. 22.—A. Mixer. B. Counterpoise. C. Gas Escape Pipe. D. Cup Elevator conveying the Raw Phosphate. E. Phosphate Reservoir. F. Balance for Weighing the Phosphate. G. Screw Conveyer. H. Feed Hopper. I. Acid Measuring Tank. KK. Underground Conveyer. L. Exit of Toxic Gases.

minutes, according to the nature of the phosphate; discharge takes half a minute. The "den" may be filled to ¾ of its height; the vacant space serves as a regulator for the evacuation of the gas. The decomposition of the phosphate by acid is effected not in the mixer, but principally in the "den" or "house". Cold acid is used, i.e. acid the temperature of which varies between 25° and 30° C. (77° to 86° F.), and of a density between 50° and 55° B. (106° to 123° Tw.). When the acid is at a lower temperature, the mixing does not heat enough to drive off the excess of water, and yield a dry superphosphate. When the acid is too hot the mixing thickens too much in the mixer, in which case the acid may be more dilute.

Owing to the evolution of gas, the thick liquid effervesces, and

forms air-bubbles which rise to the surface; at the same time it heats up to 120° to 150° C. (248° to 302° F.). Gradually the mixture settles in the "den," and after an hour it sets. An addition of dolomite (carbonate of lime plus carbonate of magnesia) keeps it liquid for sometime longer, so that the water evaporated is then much greater. The manure is also drier because magnesium sulphate crystallizes with seven molecules of water, and that is an efflorescent salt, not a deliquescent one. However, it is not usual to send a manure drier up the cups.

All the heat given off by the reaction ought to be utilized with that end in view (carrying off the water). It is only when this is done that perfect solution is realized, and that a superphosphate that will behave well on subsequent manipulation is obtained. In recent years attempts have been made to employ hot sulphuric acid and inject hot air into the chamber, in order to hasten the action and dry the superphosphate, but the results obtained proved unsatisfactory. The opinion of certain specialists may be endorsed. Such experiments will never be successful, because it is irrational to exceed a temperature of 100° C. (212° F.) in the "den" except in the case of phosphates of very good quality of which there is no need to fear retrogradation. It is better to leave the mixture to itself during its chemical transformation and allow the change to take place by insensible gradations. Experience shows, moreover, that the injection of hot air into the mass gives it the consistency of mastic, which the manure manufacturer always tries to avoid, knowing full well that the porosity of the superphosphate is the best condition to realize for subsequent operations. The construction of the decomposition house or "den" is not very complicated. The walls are two-bricks thick; they are covered inside with a coating which resists acid. To consolidate them and prevent them yielding under the pressure of the mixing, they are fortified by iron T pieces, fixed to the base by masonry, and joined to the roof by cramping irons. The roof consists of iron T pieces, three feet apart, laid on the walls, and connected together by iron rods or arches of masonry, the whole being covered by a coat of cement. All the ironwork is covered by paint to resist acid fumes. The house is fitted with a solid oak or pitch pine door consolidated inside by planks placed crosswise in the gutters. The chinks of the planks and the door are luted with a paste of clay so as to prevent air penetrating. The great difficulty with the doors is that the acid eats away the bolts of any opening handle; the men must then perforce lever it open by the pick. The result is that where the pick is applied a chink is formed which gradually enlarges. But it is not a case of air *penetrating into the house*, but of fumes from the mixer or house *escaping* into the air through chinks. Both the district authority and the Local Government Board in Great Britain would at once proceed against any

manufacturer allowing the fumes to *escape* into the air. If means be taken to prevent the *escape* of fumes, then it follows, *per contra*, that no air can gain access, because the pressure from within outwards is far greater than from without inwards. The air cannot penetrate until the gaseous fumes have condensed, and then the quality of the manure from that batch is fixed and determined It is not advisable, however, to open the door too soon, unless in the case of hurried mixing specially. The doors are best constructed of pitch pine.

In the early days of manure manufacture only one "house" was used, and the mixer was installed in the centre of the ceiling of the house; then two houses were installed with the mixer over the dividing wall between them; finally, later on, four houses have been built and the mixer placed at the junction of the party walls. This plan gives excellent results. The mixer in that case is fitted with 4 discharge doors, each of which empties into the house in which it is situated. Each "den" has a capacity of 50 to 100 tons according to the size of the factory.

Attempts have been made to devise methods of rendering phosphates soluble more rapidly and more completely than by the process just described. To accomplish this the phosphate was reduced to a very fine state, i.e. to pass through a No. 100 sieve. A paste was made with it by drenching it with water or with acid of 10° to 20° B. and finally adding the rest of the acid at 60° B. But this process was soon abandoned, for the action was found to be too violent and the metal of the mixer was attacked by the acid.

Attempts have also been made to render phosphates soluble by mixtures of hydrochloric and sulphuric acids without any great advantage. The superphosphate in this case contained 0·30 per cent of hydrochloric acid, which rotted the bags; besides, the mixture of sulphuric acid and hydrochloric acid attacks the metal.

Removal of the Toxic Fumes. The gases formed in the superphosphate "dens" cannot be allowed to escape into the atmosphere without being purified, in consequence of their offensive smell and corrosive action. They are generally passed through a wash tower by means of a fan. Benker and Hartmann make very simple installations and use for this purpose indestructible fans with washer purifiers which purify the gas completely. The fans should be rather powerful, so that the amount of air drawn into the "den" during discharge is sufficient to allow the labourers to empty the "den" under good conditions. Fig. 23 represents the tower constructed by F. Benker and E. Hartmann. It has several compartments and no packing. The gas penetrates into the first compartment, and ascending it meets a jet of water in the form of rain, produced by ebonite pulverisers (Kestner, Lille). From the first compartment they pass into the second through the top, from

the second they pass into the third through the bottom, and so on up to the seventh compartment, when they are exhausted. The silicic fluoride is decomposed by water into silica and hydrofluoric acid; the first can be separated by the filter press and the second can be concentrated to 12 to 15 per cent by volume and by mixing with alkaline chlorides, or even sulphates into the corresponding fluosilicates, which find a use in opaque glass manufacture and in flux enamelling.

The translator thinks it advisable to offer here a few criticisms

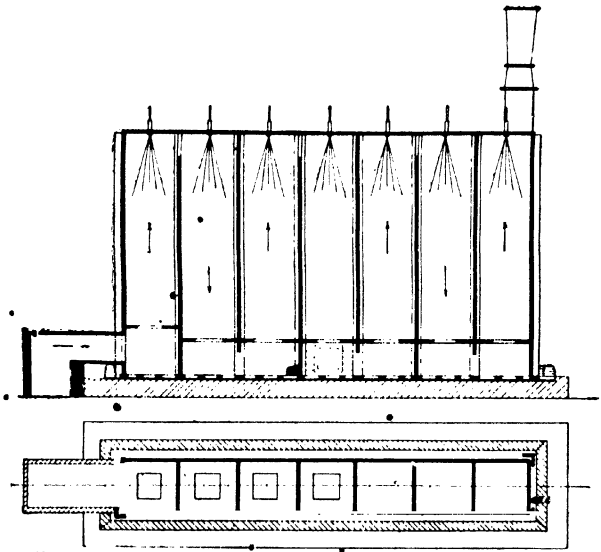

FIG. 23.—Toxic Gas Condensers (Benker and Hartmann's System).

on the method of making superphosphate as described by the author. First of all, the measuring tank has to discharge itself before it can be refilled, so the refilling cannot start before the phosphate is all in the mixer. However, it is just possible that it can be refilled in the two minutes taken up in continuing the mixing process, after all the acid and phosphate are run into the mixer—that is to say, if no hitch occurs. But if the same principle were adopted with 2 to 2½ ton mixers, as used in Great Britain, and the agitation prolonged, in accordance with the weight of the mixing, then a 5 cwt. mixing taking two minutes' agitation, a 50 cwt.

mixing ought to take twenty minutes, whereas it is shot into the "den" shortly after the last bag is up the cups and the last drop of acid run in. When the mixer is hand-fed and the lid removed, the fumes escape into the air of the building, and that is bad for the men at work. Again, a cast-iron mixer is a dead-weight on the boundary wall between the two "dens," and these, eaten away by acid, are none too strong. Again, in Fig. 22 the phosphate should all be weighed before it is shot at the foot of the cups, and the elevator should then discharge right into the mixer, and the spray of acid and the shower of phosphate should meet at the same spot. Then with a horizontal instead of a vertical mixer a wooden tank lined with 5 lb. lead can be used. The only cost is the mixing shaft and blades and the gun-metal discharge sluice valves. With such a mixer, to take $2\frac{1}{2}$ tons of superphosphate, the mixing shaft is best made in two pieces, and the middle extremities ending in projecting studs turned in a lathe are screwed up with bolts and nuts. Then if one-half of the shaft breaks the other part can remain *in situ*, and the whole shaft need not be recast. But care must be taken that the two halves revolve in perfect symmetry. Again, it is a very awkward thing to empty a vertical mixer when it sets. All that has to be done with a horizontal lead-lined mixer is to remove the (loose) boards by which it is covered and set a man at work to dig it out, and if the mixer is near the eaves all that he has to do is to remove a tile or two to secure ventilation. But in a vertical mixer, were it not for the tiny mixings described by the author, it must be a more than ordinary trying task. Coming now to hot acid versus cold acid: some phosphate can be mixed very well with cold acid, e.g. Carolina phosphate. But Somme phosphate requires hot acid, and the translator found it advantageous to keep a 10 ton tank at 140° F. This he diluted with water as required, as the author suggests. Somme is not in any way a first-class raw material.

CHAPTER VII.

CRUSHING, SIFTING, DRYING, AND STORING OF SUPERPHOSPHATE. RETROGRADATION.

Emptying and Sifting the Superphosphate House or "Den".—Emptying the superphosphate "den" is still done in a primitive manner, which consists in charging the superphosphate with the shovel into the receiving vessel of an elevator or into half-ton wagons. The latter are run towards a crane that lifts them and spreads their contents over the heap from a certain height. In

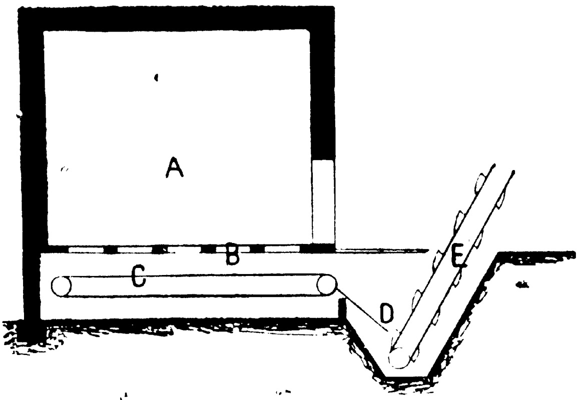

FIG. 24.—A, Superphosphate "Den". B, Discharge Apertures. C, Belt Conveyer. D, Elevator Receiver. E, Elevator.

default of the elevator the heap could not be raised high enough, and more capacious warehouses would be required. But in working even on a fairly large scale, in Great Britain the work of shifting is sometimes still done by barrow, plank, and gang sack. One man "gets" the stuff with the pick, two men fill the barrow, a fourth or fifth man, if need be, wheels it on the ground at first, then up a plank, and when the plank is too steep the barrow men cease to

ply their barrows and take to gang sacks, their heads and shoulders being protected by a "backing" cap or at a pinch by a sack.

Another method of removing the superphosphate out of the houses, consists in emptying them from below. In that case the house is built over a second compartment into which the material drops on to an endless belt 20 in. wide, through holes in the floor covered by iron lids. The belt delivers the superphosphate on to an inclined plane ending in the receiver of an elevator, which discharges the superphosphate either on the heap, into a Carr's disintegrator, or into a jigger, according to the method of working

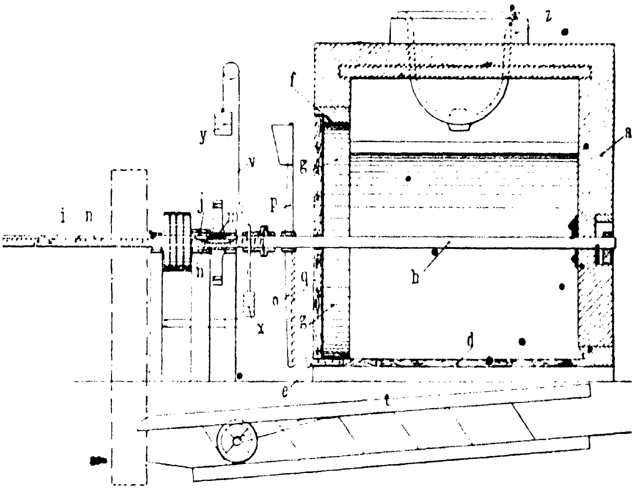

FIG. 25.—Benker and Hartmann's Mechanical Remover of Superphosphate from "Den" (longitudinal section).

adopted. The best plan is to give the elevator a certain amount of slope and use comparatively large cups, because fresh superphosphate ought to be pressed as little as possible, otherwise it is converted into a gluey mass difficult to manipulate and to dry. The emptying of the superphosphate "den" is not exactly a pleasant job, even if the heat and the gases, still persistent there and disengaged when the superphosphate is displaced, be not taken into account. The workmen are therefore obliged to use respirators, the sponge of which they should keep moist, so as to prevent any accident. The superphosphate ought to be extracted from the chamber whilst it is still hot, so that the vapour may be eliminated

and not condensed by cooling. If the superphosphate has been properly made it soon crumbles when exposed to the air; if badly made it forms lumps which do not crumble in the air, also the surfaces of these are damp from free phosphoric acid, whilst the insides form nuclei of neutral phosphate of lime: this occurs when too strong acid has been used. The core, sifted from the material, is dried in an oven if it cannot be crushed in a Carr's disintegrator.

In a general manner the reaction which superphosphate undergoes during the process which renders it soluble, and which consists in the precipitation of sulphate of lime and its conversion into

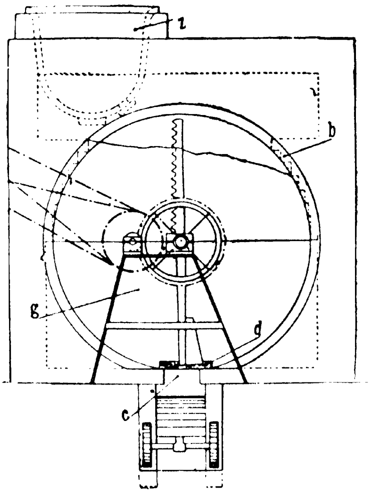

FIG. 26.—Benker and Hartmann's Mechanical Remover of Superphosphate from "Den" (end view).

crystallized gypsum, is accomplished rapidly. Certain phosphates, however, form exceptions to this rule: crystallization in this case being stimulated by stirring them with the shovel, and the process is finished by drying.

New Methods for the Mechanical Extraction of Superphosphate from the "Den".—The manipulation of superphosphate being dangerous, on account of the toxic gases which are disengaged, efforts have been made to empty the houses mechanically. But the appliances used are costly and defective, especially owing to the false position at the door of the excavation plant. Benker and Hartmann's mechanical extractor obviates these drawbacks, in so

far that the excavating organ is arranged so as to support its shaft at its two ends. Figs. 25-28 show the arrangement which forms the subject of their invention. Fig. 25 is a longitudinal section. Fig. 26 is an end view. Fig. 27 is a plan. Fig. 28 is a detail.

The superphosphate "den" *a* has interior lateral sides *b* arranged in grades, reversed above, in such a way as to give to the final block a form approaching that of a cylinder. The floor of the "den" is pierced in its centre by a longitudinal opening *c* covered by a wooden trap *d*, one of the ends of which is fitted with a ring handle *e*. The "den" has in its face a circular opening *f* shut by a door *g* in two parts. This "den" is traversed through its whole length by a shaft *h*, supported on two suitable bearings so as to dovetail into and continue a screw shaft *i* mounted in a fixed screw *j*. A cog-

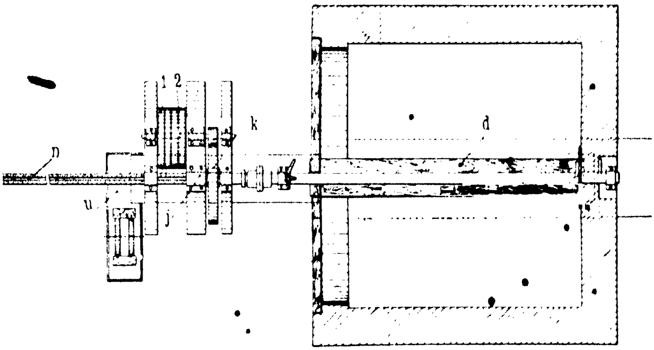

FIG. 27.—Benker and Hartmann's Mechanical Remover of Superphosphate from "Den" (plan).

wheel *k*, geared to the outside screw part of the shaft *i*, has a claw *m*, which penetrates into a longitudinal gutter *n* of that shaft, so as to connect the shaft *i* with the wheel *k* in the direction of rotation, but letting it glide freely. On the shaft *h* two arms *o* and *p* are fixed diametrically opposite one another, one of which, *o*, forms a sort of compound knife, fitted with teeth *q* projecting from the blades *r*. The other arm *p*, conveniently fixed behind the first, is fitted at its free end with a sort of shovel or spoon *s*. A conveyer *t*, of known construction, is arranged below the opening *c* of the den, and empties into a suitable elevator *u*. A band of stuff *v*, fitted with suitable counterpoises *x* and *y*, is arranged above the shaft screw *i*, so as to cover it when it enters inside the den. A mixer *z* is fixed at the top of the "den," and the installation may be

completed with fans and condensers of any desired construction. The cog-wheel *k* may be driven by any suitable means, for example, by a play of pulleys fixed and movable, 1 and 2 acting in different directions. The working is as follows: During the mixing of the mass of superphosphate the trap door *d* covers the opening *c* and the door *g* covers the circular opening in the front of the "den," the two arms, *o* and *p*, being kept outside the "den". After the superphosphate has set, the trap-door *d* is withdrawn by aid of a hand-winch, not shown on the drawings, then the door *g* is removed. The whole of the shafts, *h* and *i*, are caused to revolve in a suitable direction to bring the mechanism inside the "den". When the teeth *q* of the arms *o* come in contact with the superphosphate, it penetrates into the interior of the mass, detaching ribbons which break, forming small fragments and these fall to the bottom of the "den". The blades *r* in turn come in contact with the portion of the matter projecting between the teeth, detach these likewise in the form of

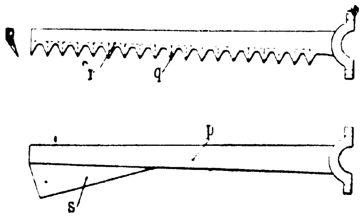

FIG. 28.—Benker and Hartmann's Mechanical Remover of Superphosphate from "Den" (detail).

ribbons, which collect at the bottom of the "den". The shovel *s* at the aperture C brings these fragments, from where they fall into the conveyer *t*. Whilst the shaft *i* is penetrating inside the "den," the cloth *v* unrolls and covers this shaft so as to prevent it being crushed by lumps of superphosphate. When all the matter in the "den" has been reduced to fragments and removed by the conveyer, the rotation of the shafts *h* and *i* are reversed, until the arms *o*, *p* are outside the "den"; the sliding door *d* is replaced as well as the door *g*, and the mixing of a fresh batch is commenced. This arrangement is simple, and economical. The arm supporting the cutting knife is fixed on a shaft supported at both ends, which prevents all work in false directions and secures a better output. The attack of the material by a vertical knife facilitates the conveyance of the fragments it forms. This arrangement may be applied to any existing "dens," best by modifying the inside shape of these "dens," so as to render them cylindrical. During the mixing of the superphosphate no delicate piece of the mechanism comes in contact with the

material, so that the mechanism is practically indestructible and little liable to damage. The screw shaft may be replaced by any other arrangement, giving to the arms *o*, *p* a forward helicoidal motion, and fitting the whole mechanism with an arrangement allowing the speed of the displacement of the arms to be increased at will; for example, for their return. The invention applies to the extraction of superphosphate as well as to manures, or analogous chemical products. Summing up, the inventors claim:—

(1) An arrangement for the mechanical removal of superphosphate consisting of a vertical shaft *o*, mounted on a horizontal axis *h*, and driven with a simultaneous movement of rotation and translation of which the blade *r* comprises projecting teeth *q*, preferably incurved on the axis, with the object of first of all bringing the teeth in contact with the material so as to commence the attack of the material by the teeth, and finish it by the blade.

(2) A method of applying the arrangement described in (1), in which the horizontal shaft *h* of the knife, comprising a radial arm *j* fitted with a shovel *s*, is supported at its two extremities and forms part of a screw shaft *i*, engaging into a fixed screw *j*, and gearing with a driving cog-wheel *k*, in which it can glide so as to avoid any false working.

Allegri's Plant for removing Superphosphate from the "Dens".—Allegri, the engineer of the united factories of the Italian agriculturists, has also patented a machine to replace manual labour in removing superphosphate from the mixing "dens". His appliance consists essentially of a sort of plough, to which a horizontal and vertical motion can be imparted. This plough traverses the chamber in the direction of its length, at each passage it detaches a thin slice of superphosphate and discharges it through the door in the top of the chamber into a conveyer. A single workman can superintend several of these machines. This machine moves 10 tons of superphosphate an hour. The force necessary is 4 H.P. The cost of upkeep is limited to changing the plough from time to time, which is the only part exposed to contact with the superphosphate. The appliance may be fitted to any existing "den" with a few alterations.

Another method of emptying superphosphate "dens" is comprised in British Patent No. 20,446 (25 Feb., 1907). It consists in the superphosphate being received on a movable platform, on which it rests so as to expose sides and top, so that the mass can be broken up in the open air. With this end in view the floor of the decomposing "den" is mounted on wheels; by this means it may be drawn out of the "den" by appropriate mechanism, through a movable door made in one of the sides. The superphosphate removed in this way is then broken up by any mechanical arrangement and charged into conveyers to be conducted to the drying

machine. Finally, the following arrangement of the superphosphate "dens," in a Bordeaux factory, is described, as an interesting improvement. The new "dens" consist of long channels in a mass of masonry work below the mixer. These channels are 1·6 to 1·8 metres above the floor of the factory. A metallic cradle placed inside these channels, of which it assumes the form, is propelled by a winch fixed on the floor on the side opposite the discharge. During mixing the superphosphate as it comes from the mixer adheres as an immense cake to the bars of the cradle. To dislodge it, it suffices by means of the winch to bring the cradle out of the den, where the product is collected in trucks. The workmen have little difficulty in detaching what adheres to the bars from whence it falls into the trucks, which they do by means of rather long tools, so as to keep at a suitable distance. A hood connected with a fan is placed on the discharge door, by means of which the fumes are drawn from the exit of the "dens," thus no inconvenience is caused to the workmen. The superphosphate is conveyed by wagons into the Persian wheels which elevate it into the drying ovens. A fan draws vapour and dust from the dryers, and propels them through a dust chamber where the dust subsides and then into a condensation tower for the removal of the acid fumes. The manufacture of superphosphate, owing to this new arrangements, presents no serious drawbacks as regards the health of the workmen or of the neighbourhood.

Breaking up and Sifting or Screening of Superphosphate.—The superphosphate placed in a heap in the fresh state consolidates itself so much that it has to be broken down or "got" by the pick and shovel. In order to reduce it to a proper degree of fineness, it was formerly projected against an inclined sieve (screen) and the "core" crushed with the back of the shovel. This sieve, of 6-8 mm. in section, that is a quarter inch sieve, is still in use in small factories. Well-made superphosphate does not require to be put through quite so fine a screen as a one-fourth inch screen except for the dry mixing of compound manures. Well-made superphosphate passed through an inch screen is fine enough for most purposes, and through half an inch for all purposes, and the price is now cut so fine that to add to the cost by passing it through a needlessly close sieve is irrational, the more so as superphosphate, as distinguished from wet mixed compound manures, has little or no core. It only wants a touch with the shovel to break it up to fine powder. Shaking and regulating sieves are also in use. To get the superphosphate from the heap, the best plan is to attack it at the tail corner by drawing it towards oneself with the pick. By lifting it in successive layers it would run the risk of being compressed. Care is taken not to excavate too deep underneath when the heap is more that 6 ft. high.

Compact superphosphate is reduced to a pulverulent state by Carr's disintegrator or a crusher fitted with steel teeth.

Carr's Disintegrator.—This disintegrator was invented by Thomas Carr of Montepelier, near Bristol, and was patented in Great Britain. It consists essentially of two, four, six, or eight

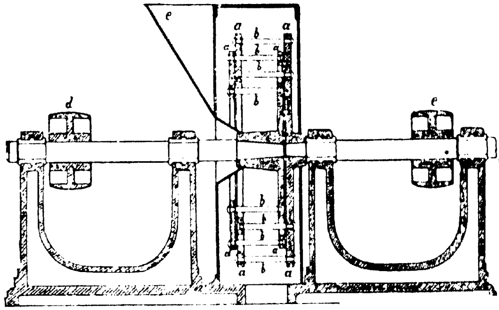

FIG. 29. Carr's Disintegrator.

concentric cages, the cylindrical sides of which consist of metallic bars *b*, encased on one side in plain discs *a*, on the other on crowns *a*. The first (inside), third and fifth cages form an aggregate of a single piece, screwed with the boss of the disc on to a driving shaft. In the same way the second, fourth, and the sixth cages form an aggregate mounted on the other shaft. The machine is driven from the same shaft by means of two belts, one of which is straight and the other crossed, so that the cages formed by one of the elements of the drum fit into the annular spaces of the other and revolve in the opposite direction. The machine is usually enclosed in a tight cover and surmounted by a hopper *e*, into which the material to be pulverized is charged. This falls into the interior cage, and the machine being in motion it is projected by centrifugal force across the bars of the first cage into the second; turning in opposite direction from the second it is projected in the same way into the third which turns in the same direction as the first, then into the fourth, and so on. Finally, it is projected on the outside on all the points of the periphery through the bars. The operation does not last a second.

FIG. 30. Carr's Disintegrator. Plan of the Cylindrical Cages.

The rapidity of the grinding is not astonishing if the great number of shocks to which the matter is subjected be considered; the power of these shocks consists in the sum of the speed of the substance in one direction and of the bars of the cage in the other. The substance issuing from the crusher falls into a side channel hollowed out of the foundation of the machine, from whence it collects in the receiving vessel of an elevator, which removes it. The size of the drums, number of revolutions a minute, the force and the number of bars, vary according to the nature and

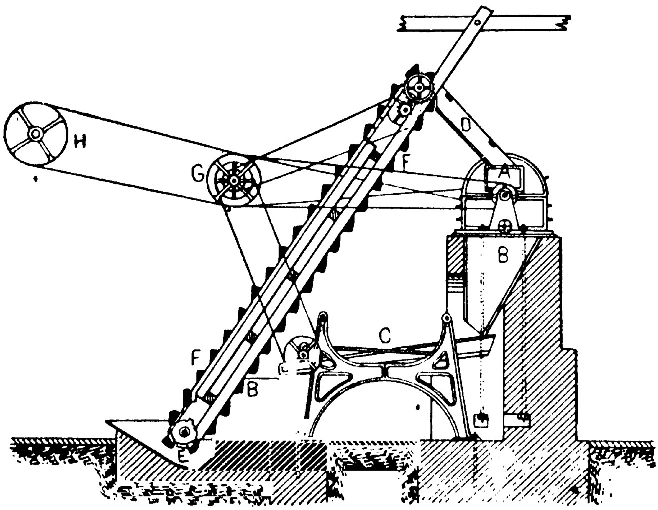

FIG. 31.—Carr's Disintegrator or Toothed Crusher. C, Sieve. F, Elevator G, H, Transmission Shafting.

the quantity of the material to be treated and according to the fineness to be imparted. A product, consisting of granules of no matter what size, can be obtained by turning the drums at a greater or less speed and having a suitable distance between the bars. The experience of the constructor is here the best guide. Carr's disintegrator is one of those which utilizes, to the best advantage, the energy which is transmitted to it, which explains its extraordinary high output compared with some of the other disintegrators. It is used, not only for crushing superphosphates, but also for degelatinized bones. It also renders good service in

making compound manures, provided that the ingredients possess the same or but slightly different densities.

Cylindrical Crusher Fitted with Teeth.—This crusher consists essentially of a cast-steel foundation, on which are mounted two rolls, one of which is smooth, and the other provided with steel teeth. The first of these rolls has a diameter of 350 mm. (about 14 in.), and travels at a speed of 100 revolutions a minute. The second has a diameter of 290 mm. (11½ in.) and revolves at a speed of 1000 a minute. This latter roll consists of a cast-steel nucleus on which are mounted toothed rings, easy to remove and replace. The machine is surrounded by a protecting cover, with a hopper, into which the material to be ground is fed. The substance passes between the rolls where it is subjected to a powerful grinding action produced both by the steel points and the differential speed of the rolls. The machine frees itself automatically from all adherent matter, which is not the case with Carr's disintegrator. It is particularly suitable for moist sticky superphosphates.

Cylindrical Crusher with two Rolls fitted with Teeth. This machine is used for the same purpose as the foregoing; it is, moreover, used in making compound manures from superphosphate and sulphate of ammonia. The two rolls have a length of 500 mm. (20 in.) by 500 mm.; the one turns slowly, the other rapidly. The teeth of one of the rolls pass into the interstices between those of the other, and thus exert a powerful crushing action on the material. It is fitted with a cover forming a hopper, and is combined with an elevator and a shaking sieve. These machines may be grouped in two ways, according to the nature of the superphosphate. The crusher may be installed at a higher level than the sieve, or on the floor. In the first case the superphosphate is fed into the receiver of an elevator which discharges it at a higher level into the hopper of the crusher. The superphosphate, after passing through the jigger, falls on a shaking sieve, the fine material passes through the sieve and falls into the discharge hopper, whilst the core in the sieve returns to the elevator, which brings it back into the crusher, and so on.

In the second case, where the crusher is fixed on the floor, the material is charged directly into the crusher, from whence it falls into the cup of the elevator which spreads it over the sieve at a higher level. The routine of the operations is absolutely the same as in the first case. But this second method has drawbacks. The cups of the elevator, in seizing the material, crush it and transform it into a sticky mass which resists sifting and returns, incessantly, from the sieve into the crusher and finally chokes up the whole of the apparatus. This drawback disappears if the machines be grouped in the manner indicated in the first instance, in which the superphosphate is elevated before being crushed; it

is then in consistent lumps which stand the action of the cups very well. The sieve itself consists of a shaking frame actuated by a to and fro motion imparted from each side by a pulley and crank. The frame of the sieve is fitted in an iron frame, on which the driving pulley is mounted. The sieve is wire woven. It must be kept perfectly clean so that the superphosphate passes through and does not return to the crusher or become sticky. If the sieve be obstructed, the machine must be stopped and the sieve cleaned. It is cleaned by beating and scraping with a broom, using sand if need be. A mechanical beater is often installed on the sieve, but it can only be used for cylindrical sieves. The latter, again, can only be used for very dry superphosphates, because in spite of the mechanical beating they become rapidly obstructed and difficult to clean.

If the superphosphate is in a pulverulent condition, it is simply sifted without being crushed; only the core from the sieve then passes through the crusher at a lower level, from which it falls into the receiver of the elevator, which spreads it again on the sieve. The elevator, crusher, and sieve act simultaneously. However, it is better to drive the crusher independently, or by an electric motor, for in many cases the core on the sieves is not bulky, and needs to be returned to the crusher only at rare intervals. It is hardly necessary to say that these machines should be easy of access. Fig. 31 represents a unit consisting of elevator, crusher, and sieve, mounted on iron frames. This unit, when fitted with rollers, may easily be conveyed from one depot to another as required. Manipulation and cost of conveyance, often heavy, are thus avoided. An installation of this nature only requires three workmen. The first feeds the cups, the second looks after the machine and bags up, the third conveys the superphosphate to the depot. In case of a break-down the three mutually assist each other. It is to be noted that damp weather is bad for grinding and sifting; the superphosphate being very deliquescent, it then adheres to the machine.

Artificial Drying of Superphosphate.—The dissolving and crushing with the machinery described above is about as economical as it can be, it is quite otherwise with the operations relating to the finishing of the superphosphate, that is to say, those that intervene between "dissolving" and dispatch of the finished pro duct. There are factories where these operations cost double wha is required in a rational installation. In the present condition of the industry, it is necessary to supplant as far as possible in effective hand labour, which is always costly, as much as possibl by mechanical methods; a machine can be stopped when desired whilst hand labour must be kept on continually, otherwise it goes. The latter, therefore, must be reduced to a minimum, the super-

phosphate finished with the least possible delay, without having to store it for any length of time to render it saleable. In this chain of reasoning, the attention of manufacturers is drawn to the machinery and processes presently to be described.

Theoretical Review of Drying.—The moisture of a superphosphate is not alone due to a high water content, but also to some extent to the presence of an appreciable proportion of free phosphoric acid in supersaturated superphosphates. Thus, when a superphosphate contains 5 per cent of orthophosphoric acid it may contain as much as 15 per cent of water, without being actually wet. According to Stocklassa, acid phosphate of lime heated to 100° C. loses, in ten hours, 1·83 per cent of water; in twenty hours, 2·46 per cent; in thirty hours, 5·21 per cent; in forty hours, 6·32 per cent; in fifty hours and upwards, 6·43 per cent constant. At 260° C. phosphoric acid changes slowly into pyrophosphoric acid,

$$2H_3PO_4 - H_2O = H_4P_2O_7$$

Moist superphosphate may be dried by evaporating the water which it contains, either by absorbing a part of the free phosphoric acid which it contains by addition of inert material, such as calcined gypsum (which combines chemically with the water), kieselguhr, peat dust, sawdust, or in fact by combining a portion of the free phosphoric acid. From an industrial point of view, we have to examine the application of heat to drying, direct heating, and cold drying. The drying machine, by direct heating, which is used for drying bones, may be used for the drying of raw phosphates, but it is not suitable for superphosphate. It is, moreover, very trying and dangerous for the health of the workmen owing to the disengagement of the acid gases of the superphosphates. Besides, the material being pressed by the workmen during shovelling, readily adheres to the plates, where it undergoes a kind of combustion from which a retrogradation of as much as 4 per cent may result. Moreover, it is very difficult to regulate the heat of a coal fire, which requires constant attention. The principal systems of drying in actual use are the following:—

Lambert's Dryer.—The inventor gives the following deliciously laconic description: The apparatus consists of a masonry chamber divided into three compartments: (1) A hearth of refractory material, in which there are mixed the hot gases from the generator hearth and the air propelled by the blowers. (2) A chamber succeeding the preceding one, into which pass the mixture of gas and hot air before entering the drying machine. (3) A stove heated by the heat radiated from the hearth, and in which the apparatus described below moves. The dryer, properly so-called, has the form of a highly-elongated truncated cone and is arranged horizontally on rollers; it is entrained by means of gearing in a

continuous system of rotation. In the interior this apparatus is fitted with corners intended to raise the material in an uninterrupted manner and to project it into the hot current during its whole stay in the apparatus. At the extremity of the small diameter of the apparatus is a feed hopper, at the other end are apertures, the object of which is to drop the dried material and allow the escape of hot air and steam during evaporation.

Zimmermann's Drying Machine.—Zimmermann's drying machine consists of an oven 8 metres (26 feet) high, heated by combustion gases. The hot air comes in contact with the material on iron plates suspended by chains and fitted with a system for agitation. An oven of this kind, occupying a space of 50 square metres (538 square feet), dries four wagons of superphosphate in twenty-four hours. The latter only remains exposed two minutes to the heat of a very bright coke fire; it then becomes heated to 80° C. and loses 5 to 6 per cent of water. The motive power required to shake the plates is three H.P., and the coke burnt, in twenty-four hours, half a ton. Three men can work two ovens. The iron plates form a drawback in not allowing the hot gases to pass, which thus take the shortest path along the sides of the oven. Lately the inventor has replaced them by sieves. The combustion gases and the acid gases pass into a dust chamber, where the latter is deposited, whilst the acid gases are purified in a condensing tower. The acid contained in the gas which is disengaged from the dryer is chiefly hydrofluoric acid. This gas, as well as the hydrofluosilicic acid, exists dissolved in the water contained in the superphosphate, and is partly re-formed when the substance is heated, any free sulphuric acid acting then on the still undecomposed calcium fluoride. The hydrofluosilicic acid is decomposed by heat into hydrofluoric acid and silicon fluoride.

The drying machine forming the object of the German patent 85,273 only differs from the above described oven in the arrangement of the interior and in the method of agitation. The shaking plates are in this case not suspended by chains, but rest on cross pieces and are moved by manuals.

Möller and Pfeiffer's Drying Machine.—Möller and Pfeiffer have constructed a drum drying machine in which they have striven to avoid shocks and sudden motion, which are absolutely injurious to the structure of the superphosphate. On the other hand, these makers secure energetic drying and ventilation by using superheated air. The apparatus is based on this principle, that each material requires appropriate treatment according to its nature. It consists of four principal parts, which are: (1) A heating system for heating dry air. (2) An exhauster for ventilating and absorbing combustion gases. (3) An arrangement for mixing air with the combustion gases and to receive the superphosphates. (4) The drum, properly

so-called. The working is as follows: The superphosphate is fed from a cup elevator into a hopper through which it falls into the drying machine, where it is met by a strong current of hot air, which forces it into the rotating drum. The current of hot air is produced by a powerful fan with a conical aperture; the jet of compressed air that issues from this aperture drives an ejector which absorbs the combustion gases. The air and the gas are mixed in varying proportions at the will of the operator, who can thus obtain whatever initial temperature may be desired. This temperature may be somewhat high without there being any reason to fear retrogradation in the superphosphate treated, for the drying of the latter being so energetic the temperature of the gas is lowered considerably. Owing to the rotation of the drum and its sloping position the superphosphate circulates to the opposite extremity and is reduced to small fragments, consequently the interior of the granules is laid bare and submitted in its turn to the action of the

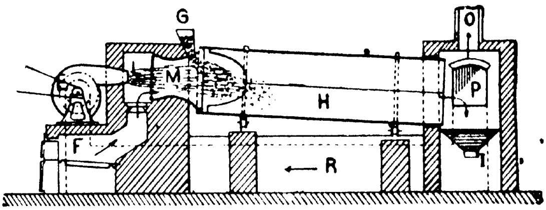

FIG. 32.—Moller and Pfeiffer's Dryer (vertical section).

hot gases. At the end of the drum the superphosphate falls into a "den," from which it is taken to be stored. The hot air which issues from the drum is not saturated with moisture; it is therefore in great part absorbed by the exhauster, mixed again with combustion gases, which bring it to the desired temperature, and afterwards it is again sent in to the drying machine, to carry on the work of desiccation. In this way the gases having already served, and still at 85° C. (165° F.) are again utilized, only the small quantity required for proper combustion being allowed to escape into the air so that fresh may come in; the loss of heat is therefore slight. However, this circulation cannot be indefinite, it is limited, naturally, by the final saturation of the escaping gases. It is then necessary to start once more with completely renovated air so as to secure regularity in the drying. This drying machine is one of the best, and has numerous applications.

Heymann and Nitsch's Process for Drying Superphosphates.—Heymann and Nitsch endeavour to utilize the heat produced by the reaction of fresh superphosphate to vaporize the water brought to

the surface of the lumps by crushing. They manage in this way to conduct drying and crushing simultaneously. The superphosphate, at a temperature of 90° C., is charged into slightly inclined rotary drums, the angle of inclination of which may be regulated at will. It is there crushed and sifted. The fine flour falls from the drum into a pit, and when it is cooled it has acquired the necessary degree of dryness. But this condition, being incapable of realization in the manner indicated, the inventors remedy it by injecting a current of hot air to meet the superphosphate as it falls from the machine into the pit. This process does not appear to have been adopted in practice.

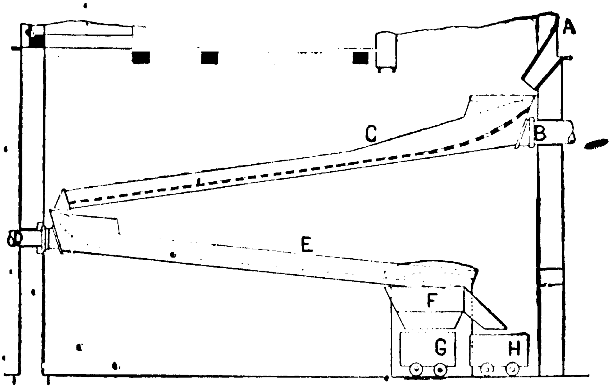

FIG. 33.—Lutjens' Superphosphate Dryer. A, Entrance of superphosphate from "den". B, Entrance for hot air under pressure. C, Drying trough. D, Entrance of cold air under pressure. E, Cooling trough. F, Sieve. G, Fine superphosphate. H, Core.

Dr. Lorenz' Process—(Dr. Lutjens' successor).—Dr. Lutjens has endeavoured to accelerate all the stages of superphosphate manufacture, the object being to terminate the whole series of operations in twenty-four hours, so that the product may at the end of that time be warehoused or dispatched. The process which he uses is kept secret, and Dr. Lutjens has refused to give the author any information. Although his process more particularly interests German manufacturers, who are obliged to make high strength superphosphates, valued according to their content of phosphoric acid soluble in water, the author thinks it his duty to give the description for the edification of his readers. The superphosphate, whilst at 100° C. (212° F.) in the "den," is taken by a conveyer on to a platform, under which a scraping machine works,

and run into the top part of the latter, through a hopper. The scraping machine, and its application, are the object of German patents 95,756 and 96,046, the author's translation of which from the original German follow, the translations at the end of the *brevet* being almost unintelligible.

German Patent No. 95,756 of 16 March, 1897. Delivered to the Chem. Fabrik Aktien Gesellschaft Vorm Carl Scharff & Co., Breslau. —The object of the new process is to divide superphosphates so as to facilitate their distribution in the soil, for, in the state of lumps, they only give up their phosphoric acid slowly and difficultly. Besides, the fine division of a superphosphate is indispensable from the point of view of the actual manner of distributing manures by the manure drill, which greatly facilitates the work of the farmer. The superphosphate, such as it comes from the mixing "den," contains about 15 per cent of water, and in that condition it is very sensitive to shocks and crushing, so much so, that the processes used to pulverize it up to now have been found unsuitable. The new process is based on this observation, that hot solid superphosphate in the state in which it exists in the mixing "den," possesses a property which has not been hitherto recognized, that of being capable of being cut into very fine slices which, exposed to the air, break up and fall to powder. The process of which the present patent is the object, consists precisely in cutting the mass in the condition in which it comes from the mixing "den" into very fine slices. Practically this is done as follows: the superphosphate is run into a drum in which knives are revolved in very rapid motion, cutting the superphosphate so as to divide it without crushing it. The thin slices are then reduced to a fine powder, the tenuity of which facilitates the expulsion of the moisture contained therein. The product thus obtained can be very easily and uniformly distributed.

German Patent No. 96,046 of 16 March, 1897. Addition to patent 95,756 of 16 March 1897, delivered 19 March, 1897, maximal duration, 15 March, 1912. The process of which this patent is the subject, is a modification of a process claimed in the chief patent, above-mentioned, the object of which is to cut up fresh superphosphate in a rotary drum armed with knives. Up to now the superphosphate from the "den" was stored, and as soon as it was cold and dry it was pulverized in a crusher. As it comes from the "den" the superphosphate is hot and soft, on cooling it becomes consistent. It has been remarked that only the superphosphate which comes from the den in lumps becomes consistent, whilst the portions that are in a pulverulent state do not agglutinate but remain in the condition of powder in spite of the pressure of the mass and the high temperature. This observation has suggested the idea that superphosphate could be reduced to a

dry and pulverulent condition as soon as it comes from the mixing "den". The crushing processes used hitherto, such as passage through a Carr's disintegrator, cannot be applied to fresh superphosphate because they would render it sticky. The present invention enables the desired state of division to be imparted to superphosphate immediately it comes from the mixing "den" without grinding or crushing it. The process employed for the purpose is based on this fact, that if superphosphate is cut into very fine slices in its original condition it is immediately converted into a fine powder. The superphosphate is transferred by a conveyer into a hopper which feeds it into a drum armed with knives. This drum consists of a posterior disc and an anterior ring. Between the disc and the ring there are arranged tangentially at fixed distances steel blades or knives, covering the openings for the exit of the finished superphosphate. Sixteen blades of this kind pass in front of the hopper aperture, at a speed of 300 revolutions a minute, consequently there are 4800 impacts per minute. The slices so produced are very fine and do not set on accumulating. The drum is driven from a shaft by means of a pulley. On the hopper side and beneath it are wrought-iron plates, on which the finished superphosphate, issuing from the drum, falls; from these plates it drops into trucks. The working of the installation is as follows: The drum is driven by a pulley and revolves at great speed. The speed, which is thus transmitted to the knives, is calculated so as to exceed the rapidity of the fall of the superphosphate into the feed hopper. In that way, all the superphosphate is forced to pass between the knives, and the uncut lumps are prevented from passing through the apertures and falling into the truck. The spaces between the knives are regulated according to the speed of the periphery of the drum and reciprocally. It follows that the knives succeed each other in their action, penetrate into the material and force their way through successive layers. Very thin slices are thus obtained which fall to powder. This division is still further favoured by the speed of rotation of the drum, which produces a strong current of air, thus acting on the substance and producing a cyclonic motion in the parts detached by the knives. The pulverized material falls from the plates into a truck. The current of air produced by the rotation of the drum imparts an impetus to the phosphate powder detached by scraping. The wrought-iron plates also serve to break this current of air in its tangential course, so that the powder only falls into the trucks at the speed it would fall by its own weight. An abrupt fall of the material is thus avoided. Finally, the current of air produced in the drum frees the superphosphate from gases which have an offensive odour, and expels them.

Dr. Lutjens afterwards modified his processes, first, in com-

bining drying with the scraping machine, afterwards in cooling the dried superphosphate. The process thus modified realizes to the letter the problem enunciated above, to produce a superphosphate ready for dispatch in twenty-four hours. For this purpose the superphosphate, cut into very fine slices, falls into an upper drying trough, where it is exposed on all sides to the action of hot air; this completely traverses the mass, heats it and renders it friable. From the upper trough the superphosphate falls into a second trough placed beneath, where drying is completed by a current of cold air under pressure, which lowers the temperature to 20° C. The superphosphate is then sifted; it quits the sieve in a very fine state, ready to be dispatched. The cold air treatment not only prevents the substance from aggregating into lumps, but at the same time prevents retrogradation, as will be seen later. The plant, it is claimed, dries 10 tons of superphosphate per hour and requires few repairs. Fuel is fully utilized, since by burning ordinary coke only 1 cwt. per 5 tons of superphosphate is required to remove 5 per cent of moisture.

It is right to add that to work regularly, this machine requires to be manned by workmen familiar with this class of work; it increases the output of the factory, and superphosphate can be dispatched from the heap. The cooling of the superphosphate was the object of the German patent No. 112,151 of 14 April, 1899, of which the following is the translation. The processes employed up to the present for drying superphosphates have the drawback of leaving these products at a high temperature, so that if run on to a heap they cool but slowly. Now, heat is very injurious to the superphosphate in the heap, and it then acquires a great tendency to form lumps. Under the pressure to which it is subjected by its own weight, it becomes compressed more strongly the longer the warehousing is prolonged and it is then necessary to pulverize it once more before dispatching it. To this drawback a graver one is added since stored superphosphate has a great tendency to retrograde, the phosphoric acid rendered soluble then returning to the insoluble condition, because heat favours retrogradation and the dried superphosphates preserve their heat when in tall heaps, and only cool slowly. The object of the present invention is to avoid retrogradation of the soluble phosphoric acid in superphosphates which have to be stored. For this purpose the heat is removed from the dried, hot, pulverized superphosphate by a current of cold air. The conveyance of the superphosphate thus finished, to the store, is done in tilting trucks or by aerial conveyer. This latter system is the best and the most economical in the manufacture of superphosphates, where it is indispensable to utilize as much as possible the covered space to store the goods. This is what a manufacturer who uses the Lutjens process says: "I

could not be better satisfied with the scraping machine. The superphosphate obtained by this process is exceedingly fine, free from lumps, and so dry that it may be dispatched a few days after it is cooled. It responds to all exigencies. Before dispatching it I pass it through a sieve of 6 mm. (a quarter inch sieve), and I get no core. The scraping machine enables superphosphates, of a quality hitherto unknown, to be made cheaply." Dr. Riemann, an expert in superphosphate manufacture, says: "We have only 0·5 to 0·7 per cent of insoluble P_2O_5 in Florida superphosphate. As a general rule we obtain an increase in the phosphate rendered soluble, and we have not observed retrogradation in Florida superphosphate even after several months' storage."

Superheated Superphosphates.—Crispo draws attention to the changes which occur in overheated superphosphates. After a certain temperature orthophosphoric acid is changed into metaphosphoric acid. Experiments on this point have shown that orthophosphoric acid, heated to 105° C. during three hours, is converted into metaphosphoric acid to the extent of 10 per cent, whilst if heated to 200° C. it is converted to the extent of 90 per cent, by the loss of a certain amount of combined water. If the soluble phosphoric acid by the citrate method be determined in overheated superphosphates, it is to be observed that metaphosphoric is not precipitated by magnesia mixture, and that only the orthophosphoric acid is found in the precipitate. If the determination be made by the molybdate of ammonia method, the sum total of the two phosphates is found, the nitric acid bringing the meta back into the ortho form. Crispo considers metaphosphoric acid of less value than the ortho. However, experiments made in Germany have shown that under the first of these two forms phosphoric acid has given good results. Experiments at the Agronomical Station of Gomblouse, by Grégoire and Hendrich, have shown :—

1. That the alterations undergone by the dried superphosphate in no way diminish the fertilizing value of that product.

2. That desiccation at a temperature of 165° C. has appreciably increased the activity of the phosphoric acid.

3. That the metaphosphate and the pyrophosphate of lime respectively, the products of dehydrating mono and bicalcic phosphates, are without fertilizing value. In pot culture experiments in the Liége laboratory, each of the pots containing 4 kilos (8·8 lb.) of soil, Ligouro oats gave, on an average, according to the phosphates used :—

TABLE XLII.—RESULTS OF EXPERIMENTS WITH ORDINARY SUPERPHOSPHATE AND SUPERPHOSPHATE DRIED AT DIFFERENT TEMPERATURES ON LIGOURO OATS.

Phosphate used.	*Grain and straw gr.*	*Proportional yield.*
Without phosphoric acid	12·3	100
Ordinary superphosphate	28·8	234
Superphosphate dried, slightly calcined	26·9	219
Metaphosphate	19·3	157
Superphosphate dried at 160° C. . .	28·8	234
,, ,, ,, . . .	27·6	224

These results show that superphosphate dried at 160° C. and slightly calcined, produce the same effects as ordinary superphosphates. On the other hand, the action of commercial metaphosphate is comparatively feeble in the sandy clay experiments. In an experiment on sandy soil the dried and calcined superphosphate had a less effect than superphosphate simply dried at 160° C. (320° F.).

Drying Superphosphates in the Cold.—Cold drying processes consist essentially in mixing with the superphosphate dry substances intended to combine with a portion of its phosphoric acid. Rumpler advises the use of bone black and degelatinized bones. These substances possess a great absorbent power and may be used with success for the drying of high strength superphosphates. As regards the use of bone dust, 1 or more per cent may be added to the superphosphate, according to its percentage of free acid. The bone dust should pass through a 70 mesh sieve. The phosphate taken from the "den" is spread out, the bone dust sprinkled over it, the mass turned over and passed through an inclined screen. After twenty-four hours the bone dust is almost all incorporated, and the superphosphate is ready to be dispatched. It is clear, however, that this work, done by hand, can only partially attain the object in view. Dr. Klippert has the merit of applying this principle, using an improved equipment, the construction of which is kept secret.

Drying of the Superphosphate by Dusting and Mixing in the Georges Crusher-Sifter.—In France an analogous process to that just described is adopted. This process consists in mixing 3 per cent of raw Gafsa superphosphate, well dried, and in the condition of fine powder. For this purpose the superphosphate from the "den" is spread by an aerial conveyer on a platform (Fig. 34); a workman dusts the product with Gafsa superphosphate and charges it into the grinding sifter shown in the figure. In this machine a shaft with blades driven at a suitable speed triturates the mass and mixes it intimately, whilst the sieve moves it in a contrary direction. The fine material falls from the sieve into the bin of an aerial conveyer which conveys it to the warehouse,

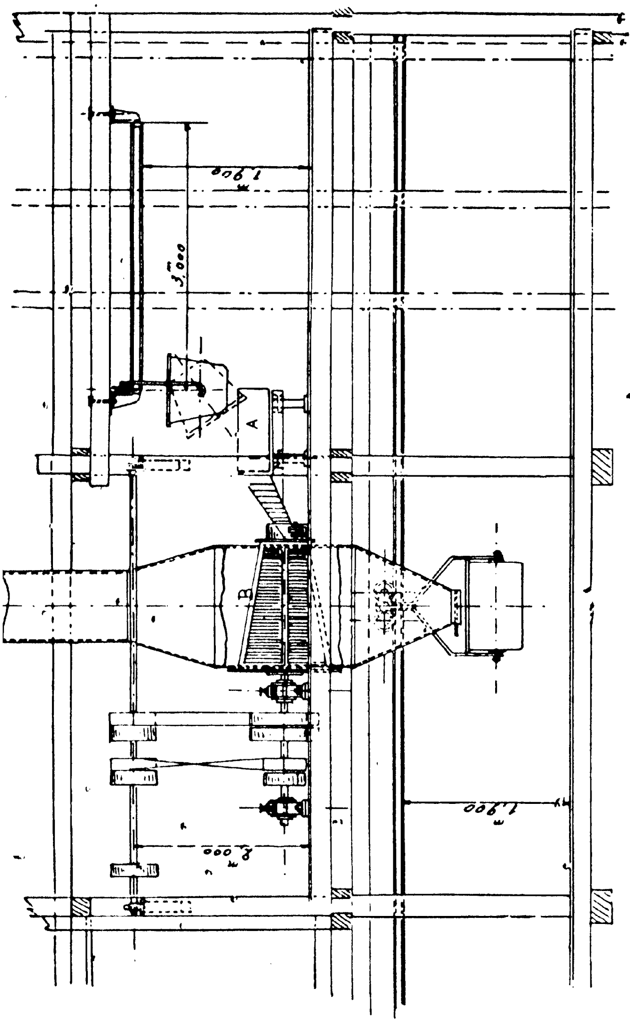

FIG. 34.—Sifting Crusher (Benker and Hartmann).
A, Table for dusting superphosphate. B, Sifting crusher (double motion), Georges system.

where it remains until the time for delivery. Before being dispatched the superphosphate is crushed and sifted through the Coster crusher. When the superphosphate is suitably prepared, the treatment indicated suffices to obtain it dry. A great number of factories have installed this process, which enables them to dispense with a drying machine. It is necessary to add that it is only applicable to superphosphates for home consumption, as superphosphates intended for exportation, especially those for the East, ought to be dried artificially in the drying machine. In the Lutjens process 1 per cent of degelatinized bones or Algerian phosphate is also added so as to dry the product and avoid the formation of lumps. The choice between bone dust and Algerian phosphate, as the drier to be added to the superphosphate, depends on circumstances. If the superphosphate is to be dispatched in a week or thereabouts, one remains satisfied with 1 per cent of Algerian phosphate. On the other hand, if it should not require to be dispatched before a month or six weeks, 0·5 of bone dust and 0·5 per cent of Algerian phosphate is added. When the phosphate has to be kept longer, 1 per cent of bone dust alone is added. The reason for this method of procedure is, that the addition of the phosphate tends to harden the superphosphate in the heap so that it has to be screened again before dispatch, or even passed through Carr's disintegrator. The new methods of Lutjens for the working of superphosphates present real advantages. But such installations being somewhat costly, they are only used where high strength superphosphates are required or when pulverulent products capable of being spread by the drill are required. It is necessary, in that case, that the superphosphate should contain an important proportion of free phosphoric acid intended to dissolve the raw phosphate added as mentioned above. A Florida superphosphate of 18 per cent, for example, should not contain more than 4 to 5 per cent of free phosphoric acid if it is not desired to add raw phosphate subsequently; if, on the other hand, 1 per cent of Algerian phosphate be added thereto, the free acid may be increased to 7 to 8 per cent. Certain foreign countries stipulate for superphosphates of very high strength. Thus Scandinavia stipulates for 20 per cent, which is nonsense, as products of this kind are really relatively dearer than 15 to 18 per cent, which are current types.

Storing (Preservation) of Superphosphate—Retrogradation (Reduction) of Phosphoric Acid. Superphosphate keeps well from one season to another when the phosphate from which it was made does not contain more than 2 per cent of the sesquioxides of iron and alumina, but it is not so if kept longer. The phosphoric acid of the superphosphate commences to retrograde ("reduce") if the raw phosphate was not pure. Retrogradation sets in much sooner if the raw phosphate contained more than 2 per cent of sesquioxides,

or if mistakes have been made in its manufacture. Retrogradation ("reduction") occurs under the influence of different causes, physical and chemical. The heat and pressure of the superphosphate heap appear to be the direct predeterminating causes. Stored superphosphate forms, first of all, packed layers. The granules of which it consists have only a slight superficial contact, but as the thickness of the layer increases the substance becomes compressed in virtue of its own weight, afterwards in virtue of the length of contact, so that finally the particles becomes cemented together to form a very compact mass. There is thus established between each an exchange of chemical energy which leads to decomposition. Experience shows that these changes are more rapid in moist hot superphosphate than in dried cooled superphosphate. The crystallization of the sulphate of lime, unfinished in superphosphate, stored hastily, is completed in the superphosphate heap. The superphosphate of lime, combining with the sulphates of the sesquioxides, forms more sulphate of lime; free syrupy phosphoric acid acts on the silicates, etc. Now, all these reactions give place to a disengagement of heat, consequently the matter expands and tension is produced. Each of these reactions occur at a fixed temperature, which it is impossible to gauge directly owing to the isolating influence of the sulphate of lime. Finally, agglutination is still further induced by the rarefaction of the air between the granules cooled in the heap. For a difference of 10° C. (18° F.) the difference is 3·5 per cent. It has been observed that the phosphoric acid of the superphosphate does not commence to retrograde ("reduce") until the moment when the particles agglutinate, i.e. when it is subjected to a certain pressure. It is, therefore, pressure which causes retrogradation by destroying the friable compounds of the superphosphate. The part played by temperature has also been determined by direct experiments. These show that it may rise to 100° C. without injuring pulverulent friable superphosphate, and up to 50° C. for agglutinated superphosphates higher temperatures are only injurious under pressure. Smetham, in examining the influence of the oxides of iron and alumina on the retrogradation of phosphates, noted an essential difference in the action of the two oxides, which had been observed for a long time in actual practice. Whilst 1 part of oxide of iron will cause nearly 2 parts of phosphate of lime to retrograde, the oxide of alumina can only retrograde its own weight of phosphate (theoretically it retrogrades nearly 3 times its own weight). In Florida phosphate, Pebbles and River phosphate, alumina forms the greater part of the sesquioxides present, but the ratio of the alumina to the iron is, on an average, 1 to 0·4. According to the same authority, iron forms two insoluble compounds, the mono-di-ferri phosphate and the di-tri-ferri phosphate; alumina only

forms one compound. The free ortho phosphoric acid would appear to be rendered insoluble in the soil more rapidly by iron and alumina compounds than monocalcic phosphate, as previously determined by Gerlach; the latter also remarks that phosphoric acid, combined with oxide of iron and alumina, does not dissolve in carbonic acid water, contrary to what occurs when the acid is combined with lime or magnesia. Phosphates of iron and alumina are only very slightly soluble in the solutions of organic acids; phosphate of iron being almost insoluble therein. As the moisture in the soil is not more acid than this artificial solution, it may certainly be taken for granted that the phosphates of the sesquioxides remain insoluble in the soil. When retrogradation commences nothing can stop it; it pursues a very rapid course, even when the cohesion of the material is broken, as is the case when orders are being dispatched. When superphosphates of this kind arrive at their destination they sometimes yield, on analysis, different results from those obtained when dispatched, but the sample then retained yields identical results, which shows that the superphosphate retrogrades even in sample bottles. Although retrogradation cannot be stopped, nor the chemical action which determines it, one can in a way prevent it in a bad superphosphate. To do this it is sufficient to dry it as completely as possible, store it cold, shorten the storage, or preserve the superphosphate in a thin layer in the beginning by spreading it over all the available space, extracting the lumps by sifting, or using it to prepare superphosphate of ammonia (the sulphate of ammonia may hinder retrogradation) or low strength superphosphates. By mixing 10 per cent of wood sawdust of bad quality with an 18 per cent P_2O_5 superphosphate which had retrograded 1·5 per cent, it was observed that the phosphoric acid did not retrograde further in the low strength manure thus prepared. In this case the amount of liquid contained in the superphosphate $H_3PO_4 + H_2O$ lost 45 per cent of its mobility in consequence of this dilution. On the other hand, the superphosphate was relieved from its pressure, the latter being spread over all the ballast. It is clear that this remedy has limits but it gives good results.

Forestalling Retrogradation by Schucht's Method. To ascertain if a superphosphate is liable to retrograde, and at what moment it will retrograde, are points which it is important for the manure manufacturer to determine. Schucht has used for years a method which gives results agreeing substantially with facts. It is generally very difficult to get access to the lower layers of a superphosphate heap. It is, therefore, impossible to analyse them, and another means of control must be found. This means is supplied by the retrogradation indicator about to be described. The apparatus consists of a graduated lever a (Fig. 35), on which is a movable runner

of 15 kg. (33 lb.). This lever is movable upon a point of support *b*, fixed on a fork *c*. A very strong flat-bottomed porcelain vessel *e* is used to receive the superphosphate, which is compressed by means of the plug *f* fixed on the lever. The operation is conducted as follows: 100 grms. of superphosphate are run into the porcelain dish with 25 grms. of hot water, and the mixture crushed with the pestle; the excess of water is expelled on the water bath and the vessel is put under the press plug, which compresses the contents of the dish. The apparatus is kept under pressure for twenty-four hours at a temperature of 50° to 70° C. (122° to 158° F.), water soluble phosphoric acid and free phosphoric acid are estimated in the superphosphate, treated as above, after having already made the same estimations in the original superphosphate. By comparing the results of the two analyses a valuation of the superphosphate can be made. The differences existing between manufacturing

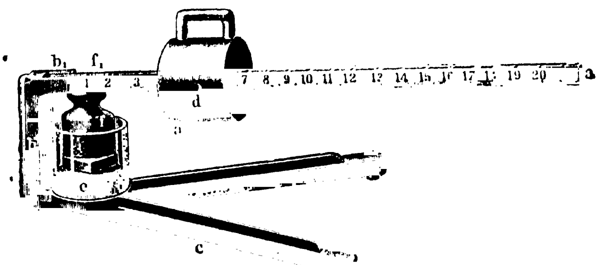

FIG. 35.—Retrogradation Indicator (Schucht).

localities and in storing in no way influence the accuracy of the method. If the exact temperature and pressure be found, they remain the same in all cases so long as the raw material is not changed. This method is far from solving the question of retrogradation, but it is interesting, because an idea can be gained from it of the retrogradation of a given phosphate. Dr. Grueber gives the results of experiments which he has made with Schucht's apparatus, of which the following is a brief summary:—

1. A Florida phosphate, 35 per cent P_2O_5, and 2·52 of sesquioxides, when rendered soluble gave 18·7 per cent P_2O_5 soluble in water, and 1·21 of insoluble P_2O_5. Treated after Schucht's method, under a pressure of four atmospheres and at a temperature of 40° C. (104° F.) (the apparatus being home-made could not do better), it contained 18·2 per cent of P_2O_5 soluble in water, and 1·76 of insoluble P_2O_5. A second Florida phosphate, with 35·96 per cent P_2O_5 and 2·38 per cent sesquioxides gave immediately

after being rendered soluble, 18·8 per cent P_2O_5 and 0·81 insoluble. After Schucht's treatment it yielded 16·67 per cent soluble P_2O_5, and 2·62 per cent insoluble, which shows the efficiency of Schucht's apparatus, that is to say, that the particles of phosphate, intimately mixed and pressed hot, show an accentuated tendency to retrograde.

2. A comparison was made with a superphosphate stored hot in a large heap. A Florida phosphate with 35·8 per cent P_2O_5 and 2·09 per cent of sesquioxide, was in use. This phosphate, tested immediately after being "dissolved," gave 18·40 per cent P_2O_5 soluble and 1·1 per cent insoluble. With Schucht's method it gave 17·25 per cent soluble P_2O_5, and 2·06 per cent insoluble. The stored heap showed at the end of a year 17·28 per cent P_2O_5 and 1·96 per cent insoluble. Consequently the stored phosphate confirms the accuracy of Schucht's method. Half way down the heap a retrogradation of only 0·21 per cent occurred and no retrogradation had taken place in the upper portion.

3. Another experiment was made with a Florida phosphate, with 35·49 per cent P_2O_5 and 2·25 per cent of sesquioxides. When "dissolved" it gave 18·98 per cent of soluble P_2O_5, and 0·95 per cent of insoluble. Schucht's method was applied in three ways, using a Schucht's instrument constructed by Kohler and Martini of Berlin, by which a higher temperature and pressure could be applied, the following being the results:—

(*a*) Pressure and average temperatures as above: 4 atmospheres pressure at 40° C., 17·09 per cent soluble P_2O_5, 1·85 insoluble; (*b*) increased pressure and average temperature: 7 atmospheres pressure at 40° C., 16·67 per cent soluble phosphates, and 1·91 per cent insoluble; (*c*) increased temperature and pressure: 7 atmospheres pressure at 70° C., 16·72 per cent soluble P_2O_5, and 2·28 per cent insoluble. This superphosphate, though piled in a heap 16 ft. high, did not retrograde even in its lower part, which Dr. Grueber attributes specially to the storing of the superphosphate, after complete cooling, by Dr. Lutjens' scraping and cooling appliance. The fact that the cooled superphosphate did not retrograde is not surprising, because as far back as 1870 the important fact was observed in the case of superphosphates made from Lahn phosphorite, very liable to retrograde, that the more rapidly it was cooled the less the soluble phosphoric acid retrograded. Dr. Grueber concludes that, in order to explain retrogradation, decisive results will only be obtained by working on the large scale with superphosphates to which different materials have been added. With the data so obtained, the treatment of phosphates could be modified according to their composition and the manner in which they behave.

Dr. W. Paysan considers retrogradation is a rather exceptional

phenomenon. He supports his view by personal experiences with Algerian phosphates with 0·5 of sesquioxides, and Peace River Pebbles with 2·5 per cent of sesquioxides. The solubility of the first was always carried in a constant manner to 0·75 per cent of insoluble, that of the second to 1 per cent. He never found retrogradation in either, even after long storing. He considers that in valuing phosphates too much importance is attached to the percentage of sesquioxides. To prove it he quotes trial mixings he made with this end in view. In this case three Tennessee phosphates (*a*), (*b*) and (*c*) were used, containing 79 per cent phosphate of lime, 2·36 per cent oxide of iron, and 2·24 per cent of alumina, say a total of 4·6 per cent of sesquioxides. The results are given in the following table:—

TABLE XLIII.—SHOWING CHANGES IN COMPOSITION WHICH TENNESSEE SUPERPHOSPHATES UNDERGO IN FOUR AND A HALF MONTHS FROM DATE OF MAKING.

	P_2O_5. Insoluble.	Soluble.		Insoluble.		Free Acid.
		Al_2O_3.	Fe_2O_3.	Al_2O_3.	Fe_2O_3.	
Mixings made, September 2, 1898	(*a*) 2·27	0·90	0·26	–	– –	5·50
	(*b*) 2·20	1·07	0·27	– –	1·05	5·50
	(*c*) 1·98	1·28	0·29		1·01	6·10
Sample of same superphosphate, analysed November 17, 1898	(*a*) 2·35	0·65	0·17	–	1·21	4·20
	(*b*) 2·33	0·87	0·18	–	1·20	4·30
	(*c*) 2·32	1·09	0·22		1·17	4·80
Sample of same superphosphate, analysed January 17, 1899	(*a*) 2·30	1·14	0·17	–	1·0	4·90
	(*b*) 2·23	1·08	0·22		1·12	4·80
	(*c*) 2·48	1·22	0·16	– –	1·12	5·30

Paysan adds that not being able to trace the cause of retrogradation to the sesquioxides, he sought for it elsewhere, and he quotes the following case of a delivery of Florida phosphate. The samples taken the first day at four different points looked well; the next day fresh samples were taken, this time going further forward than the points explored the day before; it was then found that in certain places the phosphate was darker than in others, and contained much impurity. Two samples of this kind, taken at two different points, gave the following figures:—

	a Per cent.	*b* Per cent.
Phosphate of lime	71·97	64·65
Sand	8·85	19·00

An average sample of the whole cargo gave the following analysis. Phosphate of lime 77·73, oxide of iron and alumina 2·13 per cent. The pure phosphate behaved in a normal fashion. In working it dissolves completely and gives no retrogradation, but when mixed with the impure part retrogradation took place rapidly, 1·52 to 2·14 per cent of insoluble was obtained against 0·75 with the pure superphosphate. This example well explains contradictions and obscure points. But Dr. Paysan does not admit the effect of pressure in the question of retrogradation. He has often remarked a tendency to retrograde in superphosphates as soon as they have gone through Carr's disintegrator. He does not ascribe transcendent merit to Dr. Lutjens' processes. He regards them as elegant and useful auxiliaries in superphosphate manufacture, but which do not dispense with passing the manure through Carr's disintegrator. A 25 per cent soluble phosphate, say phosphoric acid = 11·45 per cent, is the current British make of soluble phosphate. A 12 per cent Somme will give a 30 per cent soluble phosphate which will bear an addition of 3 cwt. of gypsum to the ton to bring it down to 25 per cent if the superphosphate is dispatched as soon as made. Or the gypsum may be partially replaced by a little Belgian phosphate. But in Britain it is not considered good business policy to add a nitrogenous manure like bone dust to a superphosphate, and the tendency of the workmen is always to use far more bone dust than that in the formula, for reasons which will be readily appreciated ; the result being that when it comes to stocktaking the leakage of bone meal and bone dust is excessively large. What the translator cannot understand is the magical effect of 1·0 per cent of bone dust, say one-fifth of a cwt., i.e. 22 lb. to the ton. If the superphosphate was very damp such a pinch of bone meal would be a drop in the ocean ; 3 per cent of raw Gafsa phosphate can be understood. It will readily be seen that only by strict book-keeping by double entry can the amount of phosphate and bone dust used as driers be controlled. The translator fears the author is somewhat over-sanguine as to the efficacy of some of the drying machines and grinding machines which he describes. It appears to the former that if a manure will dry naturally, as it should do, these machines are not so indispensable as would be inferred, and where the manure will not dry naturally one may be pardoned from doubting if the machines are quite so efficacious as one is led to believe.

Basis on which Superphosphates are Sold.—In the beginning of the superphosphate industry, superphosphates were sold according to their percentage of phosphate of lime soluble in water. But there were disputes between buyers and sellers, the former not finding the strength given them by the latter. A portion of the phosphate had become insoluble on delivery. The British were the

first to determine that the part of the phosphate originally soluble in water, and at the end of a certain time was no longer so, was, however, soluble in weak reagents, such as carbonate of soda or oxalate of ammonia, whilst the phosphate, originally insoluble, did not dissolve appreciably in these reagents. At first it was thought that this phosphate which British chemists called "reduced" phosphate but now term retrograde phosphate, was formed by the action of the monocalcic phosphate on the tricalcic phosphate producing an intermediate bicalcic phosphate. Such, at least, was the current explanation twenty years ago. Be that as it may, manufacturers have got over the difficulty, not by improving their manufacture but by altering the basis of sale of superphosphates, i.e. by selling them according to their content per cent of phosphoric acid soluble in cold alkaline ammonium citrate, which they term assimilable phosphoric acid. This method of sale is evidently very convenient for the manufacturer, and enables the works chemist to cease from worrying over retrogradation whether it arises from bad manufacture or the presence of impurities in the raw phosphates.

Now, as Mr. J. Joffre observes: "When a superphosphate is treated with citrate of ammonia for the purpose of analysis, both the citrate soluble phosphoric acid, and the water soluble phosphoric acid, enter into solution simultaneously. It results that when the analysis is made by the citrate method (without a separate estimation of the phosphoric acid soluble in water) there are confused together both the phosphoric acid soluble in water, of great fertilizing value, and the phosphoric acid combined with iron, which has but very little. The citrate method is, therefore, uncertain. The results may represent products which are very good for plants if they consist of monocalcic phosphate or free phosphoric acid which are dissolved in this reagent. They may, on the other hand, represent substances which only have a very mediocre action, if they are phosphates of iron, called retrograde phosphates, which have passed into solution. Analysts ought, therefore, to give preference to estimating by the solubility in water as in Great Britain, Germany and the United States. They ought, at least, to estimate separately the portion soluble in water and likewise separately the citrate soluble."

It is now admitted, however, that there is no great difference from a fertilizing point of view between the water soluble phosphoric acid and the citrate soluble. There is, however, a sharp line of demarcation between the two products; the first is immediately assimilable by plants, the second is rendered soluble and assimilated in the soil to the same extent as the phosphoric acid in basic slag. But that being the case there is no occasion for the difference in price between the selling price of superphosphates (supposing them to be partially retrograded since they are sold as such) and basic slag. Now this difference is considerable. On

1 January, 1909, for basic slag at Paris stations the price of the unit of phosphoric acid in basic slag and superphosphates was exactly in the ratio of 3 to 4, which makes the phosphoric acid in retrograde phosphates 25 per cent dearer than the citrate soluble phosphoric acid of basic slag. It is asserted, it is true, that if retrogradation has not already occurred in the superphosphate before spreading it occurs rapidly in the soil. The validity of this assertion will be examined later on in giving Dr. P. Wagner's opinion on the matter. In Germany superphosphates are sold according to their content per cent of water soluble phosphoric acid, the citrate soluble not being taken into consideration. Now, in superphosphates containing 1 per cent of insoluble phosphoric acid, this latter being two-thirds soluble in water, the manufacturer is prejudiced to that extent. In Spain and in the Mediterranean regions the customs are the same as in France. In Austria-Hungary customs vary with the localities; in some parts superphosphates are sold according to their content of water soluble phosphoric acid, in others according to their content of citrate soluble. It is the same in Russia. In America sales are also based on the citrate soluble which enables manufacturers to work low-grade phosphates with a high percentage of sesquioxides. At present Germany manufactures more chemical manures than any other country in response to the increasing demands of agriculture.

Phosphatic Manures—Do they become Insoluble in the Soil?—The benefits of enriching the soil in phosphoric acid has sometimes been questioned on the ground that phosphatic manures become insoluble in the soil, and consequently inactive in a period of time varying from one to three years. This objection has been refuted by Dr. Wagner. If superphosphate or basic slag be buried and the soil be left to itself without tilling it or sowing it, what happens? The result will be that the rain, filtering through the layer of soil, will insensibly dissolve the phosphoric acid of the superphosphate and the basic slag, and will transport it always a little further into the subsoil, where it comes in contact with oxides of iron, alumina, and lime. It will combine with these oxides, forming less and less soluble compounds, to pass finally after fifty or a hundred years perhaps, one does not know exactly, to almost the same state of insolubility as the phosphoric acid contained in the minerals in the soil.

"This transformation will require a very considerable time. It is also certain that in a cultivated soil, tilled, sown, and manured, the processes of solution unceasingly oppose the tendency to become insoluble; the cultivated soil opposes the contrary one, that of becoming soluble. The humic acid, the carbonic acid, the nitrate of soda, the roots of plants, fungi, bacteria, the circulation of air and moisture, are constant agents of activity which do not allow the soluble phosphoric acid to come to rest. As soon as precipitated phosphates are formed in the soil with a portion of the phosphoric acid, whether from superphosphates or basic slag, the agents in the

soil just enumerated exert their solvent action and bring back the phosphoric acid to the soluble state, the lime, alumina, and oxide of iron reprecipitate it again in part, the agents in the soil bring it back unceasingly to the soluble state, and so on. The phosphoric acid, therefore, is not at rest in the soil; it passes from one state of combination into another; it unites to one element for a fleeting union and quits it to unite to another element to form a union quite as ephemeral, for the agents of combination and solution contained in the soil are engaged in an incessant struggle to seize and carry away the phosphoric acid for themselves; sometimes it is the one, sometimes the other, that remove it in a transitory fashion. But the phosphoric acid retains its instability. The more intensive the culture, the more the soil is aerated, rich in humus, the more abundant the manuring with nitrate, ammoniacal and potash salts, the deeper the tilth, the heavier the crops, the less chance has the phosphoric acid in excess entrusted to the soil of passing to the insoluble state, at least in large enough amount to occasion fears as to its action."

In support of these arguments Wagner relates the results he obtained with experiments on basic slag on a meadow, poor in phosphoric acid, which yielded only about 1½ tons of hay per hectare (12 cwt. per acre). A series of plots received 800 kilos of basic slag per hectare, i.e. 704 lb. per acre on 30 October, 1889, another series remained unmanured. As an auxiliary manure the same amount of kainit was applied each year. The phosphatic manure was not renewed. The 800 kg. of basic slag per hectare (704 lb. per acre) applied once have produced:

TABLE XLIV.—SHOWING FOR A SUCCESSION OF YEARS THE INCREASE IN HAY FROM ONE APPLICATION OF BASIC SLAG TO A POOR MEADOW.

Year.	*Increased yield.*
1890	750 kilos of hay per hectare
1891	2300 ,, ,, ,, ,, ,,
1892	2600 ,, ,, ,, ,, ,,
1893	1440 ,, ,, ,, ,, ,,
1894	2930 ,, ,, ,, ,, ,,
1895	1310 ,, ,, ,, ,, ,,
1896	1060 ,, ,, ,, ,, ,,
1897	920 ,, ,, ,, ,, ,,
1898	570 ,, ,, ,, ,, ,,
	13,880

The manuring with 800 kg. per hectare (704 lb. per acre) of basic slag, once applied, continued to act during nine consecutive years, and produced during this interval an increase of 13,880 metric tons of hay per hectare, say 5 tons 12 cwt. per acre. In this experiment it is evident that the basic slag has not been rendered insoluble, and the reserve of manure entrusted to the soil has been

fully available. It goes without saying that this experiment, by itself alone, ought to afford instruction as to how a phosphate manure once applied behaves in its restorative action, for to entrust a soil with a reserve of manure, and to allow this manure to act for nine years without restoring the amount consumed by vegetation, is a very severe test: moreover, other experiments in different directions have shown that a yearly application of manure still further increases the yield. It is hardly sound or logical reasoning, however, to assume that the action of basic slag in the soil is the same as that of superphosphate. This meadow possibly was sour and wanted lime, which basic slag supplied. Part of a 25-acre field was limed, then planted with Scots pine; the pasture under the trees on the limed portion was easily differentiated by its excellent quality 40 to 50 years afterwards from the almost bare unlimed portion.

Dr. Edward John Russell in a paper on artificial fertilizers[1] gives the following figures showing the improvement in the composition of superphosphate due to the use of richer mineral phosphates:

	P_2O_5 per cent.	*Equivalent to* $Ca_3H_4(PO_4)_4$.
30 or 40 years ago	9·1	20
20 years ago	11·8	26
Modern samples	13·6 16·0	30 35

The production of superphosphate in metric tons in 1903 to 1910 is given by the Institute Internationale d'Agriculture, Rome, as follows:—

	1903.	1904.	1905.	1906.	1907.	1908.	1909.	1910.
France	1,053,000	1,234,800	1,314,000	1,320,300	1,632,600	1,848,600	1,641,600	1,634,400
Germany	765,000	831,600	873,000	837,000	1,105,200	1,191,600	1,267,200	1,353,600
Italy	392,400	453,600	455,400	595,800	797,400	1,020,600	928,800	806,400
United Kingdom	655,200	689,400	772,200	786,600	909,000	937,800	807,300	756,900
Belgium	208,800	223,200	234,000	208,800	234,000	334,800	349,200	394,200
Holland	208,800	280,800	288,900	274,500	286,200	354,600	352,800	385,200
Total Europe	3,559,500	4,043,880	4,321,980	4,451,400	5,563,080	6,402,500	6,008,400	6,105,600
Total America	1,452,[illegible]00	1,665,000	1,710,000	1,652,400	2,046,600	2,210,400	2,304,000	2,858,400
World's Total	5,130,900	5,863,500	6,281,024	6,463,440	8,003,880	9,158,300	8,710,200	9,604,260

The figures for the United Kingdom are estimated, since reliable data are not available. Some authorities estimate it at over 1,000,000 tons.

[1] "Jour. Soc. Chem. Indt.," 1917, p. 250.

CHAPTER VIII.

COMPOUND MANURES.

Manufacture of Mixed Manures.—The manures generally used for admixture with superphosphates are Peruvian guano, bone dust, sulphate of ammonia, and nitrate of soda, but the Peruvian guano dispatched from the localities of production now is much less rich in nitrogen than that imported in the past. Its place is taken by sulphate of ammonia, ground horn, dried blood, dried meat, etc. Superphosphate of potash is also prepared. The mixing is done as much as possible after the phosphate is dissolved. Mixing is not done in the dry state, except when it cannot be performed otherwise.

In the wet mixing of compound manures where such things as sulphate of ammonia, meat meal, fish guano, bone meal, kainit, sheddy, etc., go up the cups, retrogradation is less marked. The other ingredients apparently, at least, retard retrogradation, if they do not prevent it to a great extent. A 30 per cent soluble phosphate which retrograded 3 to 4 per cent in a few months when dry mixed, so as to give 20 per cent soluble phosphates and 7·0 per cent ammonia, maintained that composition exactly for several months in a 250 ton heap. It is better to use up superphosphates with such a marked tendency to retrograde in the making of wet mixing compound manures.

Hand labour is the best for this kind of work. The materials, previously weighed and sifted, are made into a 2 ton heap by means of a barrow capable of holding 100 kilos (2 cwt.). To turn the matter properly the shovel is plunged into it vertically, so as to mix it, then after having sifted it, it is made into a heap in the inverse order, that is to say, by lifting it from the ground to throw on to the middle of the heap.

The following explanation will make this plainer:—

Take a 10 ton mixing according to the following formula:—

	Tons.	Cwts.
15 cwt. superphosphate	— 7	10
3 cwt. sulphate of ammonia	— 1	10
1 cwt. bone meal	—	10
1 cwt. muriate of potash	—	10

First of all the 7½ tons of superphosphate would be laid down in a heap and accurately levelled, then the 1½ tons of sulphate of ammonia would be spread uniformly over the levelled top of the heap, then the ½ ton of bone meal uniformly over that, then the muriate over that. Then a screen with two men would be placed at one end of it and a man to get the stuff for them, that is by digging down the heap vertically and mixing it for the two men to shovel it through a ½ inch or 1 inch screen. When this first screening is done the material is screened through in the reverse direction, but this time through a ¼ inch sieve. If the heap has been laid down anything like proportionately and uniformly, samples taken from any point will agree in analysis in a manner that those who have not seen it done would hardly credit. If the 7½ tons of superphosphate were taken from the superphosphate heap, if the foreman has a good eye for bulk and weight, there need be no necessity to weigh the 7½ tons; he can tell to a nicety its bulk.

The British manure manufacturer works in cwts. to the ton, thus a very easy calculation shows that 8¾ cwts. of sulphate of ammonia (of 20·5 per cent. N) to the ton mixing, gives 9 per cent of nitrogen in the mixing; a similar easy calculation shows 11¼ cwts. of superphosphate with 35 per cent of soluble phosphate to the ton mixing, gives as near as may be 19·647 per cent of soluble phosphate in the mixing, and 19·647 of soluble phosphate is equal to 9 per cent of soluble phosphoric acid ($9 \times 2·183$).

These manipulations are sometimes rather unpleasant, such as the disengagement of dust, etc., nevertheless they form the best method of mixing. The materials so mixed are afterwards passed through a Carr's disintegrator or through the toothed crusher, a very homogeneous mixture being thus obtained. Inert materials should if possible be avoided in these mixings. By mixing high strength superphosphates with low strength superphosphates common sorts can be made without recourse to inert materials, sand, plaster, etc.

In mixing, however, it is often impossible to avoid the use of gypsum, the more so as it dries the manure and gets the core through the screen. To get the core in this case through the screen with bone dust would be a waste of money, as apparently no value is attached to insoluble phosphate. Supposing the superphosphate used tests in this case 38 per cent. of soluble phosphate, it is a clear case for the addition of gypsum instead of using two grades of superphosphate. Moreover, a manure of this nature with neither potash nor bone meal would have no backbone.

Ammoniated Superphosphate.—Although the composition of this manure is very variable, the most usual strength being 9 : 9, 5 : 10, or 6 : 12, the first figure indicating the percentage of nitrogen, the second the percentage of soluble phosphoric acid, this manure is in great esteem. It is analogous to dissolved Peruvian guano to

which farmers are accustomed. Moreover, it presents the advantage, that its acid retrogrades less easily in the soil than that of pure superphosphate, seeing that the sulphuric acid combines first with the bases which it encounters in arable land. The mixture of superphosphate with sulphate of ammonia is easily made. Sulphate of ammonia is delivered in a finely ground granular condition. It contains 24·5 per cent of NH_3 = 20·2 per cent N and about 1 per cent of moisture, which is an advantage for the manufacturer, for the mixtures 9 : 9 have to be delivered with a maximum of 6 to 7 per cent of moisture, those of 5 : 10 with a maximum of 8 to 9 of moisture, in order to obviate the formation of lumps in the sacks. To obtain very homogeneous ammoniated superphosphate the sulphate of ammonia is added during the "dissolving" of the superphosphate by dissolving this salt in the sulphuric acid used to decompose the superphosphate, but this method of proceeding is not applicable except with small amounts of sulphate of ammonia; with large amounts it should be mixed later.

The process generally used in making ammoniated superphosphate is as follows: The dry superphosphate and sulphate delivered in 10 ton wagons, being stored and analysed, the amount of superphosphate and sulphate required to give a mixture of 9 : 9 has to be calculated. Suppose that the sulphate of ammonia contains 20·5 N, then 20·5 kg. correspond to 100 kg. $(NH_4)_2SO_4$, 9 kg. correspond therefore to $\frac{100 \times 9}{20 \cdot 5} = 42$ kg. $(NH_4)_2SO_4$. There remains then for the superphosphate 100 − 42 = 58 kg. These 58 kg. of superphosphate must contain 9 kg. of soluble phosphoric acid, which corresponds to $\frac{100 \times 9}{58} = 15 \cdot 5$ per cent of phosphoric acid. To make the mixture the 10 metric tons of sulphate of ammonia are laid in a heap 33 ft. long and on each heap the necessary portion of superphosphate to the total of 13·81 metric tons. Two labourers mix the two with the shovel, making the whole into one heap and recommence the same in an inverse direction. The mixture is then passed through Carr's disintegrator or the toothed crusher, after which it is laid on a big heap in the warehouse for the ingredients to combine.

Mixtures of superphosphate and sulphate of ammonia exhibit phenomena of a peculiar nature. They gradually heat and become damp to the touch; they dry again, and, owing to the formation of gypsum, they harden more and more. The reaction lasts for a variable time. It depends on the nature of the superphosphate and its manner of manufacture, and may end in fifteen days, when the mass is in a large heap, and exposed to a certain pressure. Ammoniated superphosphate forms a hard, sometimes rocky mass, the

handling of which is expensive, but in order to prevent it setting too hard 1 to 2 cwts. of bone meal may be added to each ton which keeps it open and friable. It is crushed by Carr's disintegrator, is passed through the sieve, and bagged up immediately afterwards, for it does not solidify again if made in a proper manner. To diminish the hardening as much as possible, sand, or better still, powdered peat, sawdust, wool dust, or chimney soot may be added, and in the second place, immediate saturation of the sulphate of lime by the addition of a little water. The second grinding is therefore necessary to effect the perfect mixing of the two ingredients. In fact, if the substance be analysed after the first crushing, there may perhaps be found 8·8 per cent of phosphoric acid and 9·2 per cent of nitrogen, together 18 per cent, but after the second crushing the product uniformly shows 9 per cent of phosphoric acid and 9 per cent of nitrogen. A similar method of calculation serves, equally, for all the mixings, thus for ammoniated superphosphate 5 : 10. For 100 kg. of mixture, take $\frac{100 \times 5}{20{\cdot}5} = 24{\cdot}4$ kg. of sulphate of ammonia of 20·5 per cent N, and consequently 75·6 kg. of superphosphate containing $\frac{100 \times 10}{75{\cdot}6} = 13{\cdot}2$ per cent phosphoric acid. If a wagon of 10 tons of sulphate of ammonia is to be used, 41 tons of the mixture will be obtained of the 5 . 10 mixture, requiring consequently 31 tons of superphosphate. It is easy to bring the superphosphate to the right strength by diluting a high-strength superphosphate with a low-strength superphosphate or with gypsum free from iron, alumina, and carbonate of lime, or enriching a poor superphosphate with a rich superphosphate, or with a double superphosphate.

Superphosphate with Sulphates, Ammonia, and Potash Salts. This mechanical mixture of sulphate of ammonia and potash salts with superphosphate is prepared in a similar manner. Suppose it is desired to prepare a mixture of this nature containing 5 per cent of nitrogen, 7·5 per cent of potash, and 9 per cent of phosphoric acid, and that the ingredients to be used for the purpose are sulphate of ammonia with 20·5 N, and potash salts with 37 per cent K. To produce 100 kg. of such a mixture it would therefore be necessary to use:

$$\frac{100 \times 5}{20{\cdot}5} = 24{\cdot}4 \text{ kg. of sulphate of ammonia.}$$

$$\frac{100 \times 7{\cdot}5}{37{\cdot}0} = 20{\cdot}3 \text{ kg. of potash salt, and consequently}$$

55·3 kg. of superphosphate testing.

$$\frac{100 \times 9}{55{\cdot}3} = 16{\cdot}27 \text{ per cent of phosphoric acid.}$$

TABLE XLV.—NUMBER OF CWTS. REQUIRED IN A 5 TON MIXING, OR OF TONS IN A 100 TON MIXING OF A SUPERPHOSPHATE OF A GIVEN STRENGTH IN P_2O_5 TO PRODUCE A MANURE OF A GIVEN STRENGTH IN P_2O_5.

P_2O_5 in the Super-phosphate.	P_2O_5 in the Mixture.											
	8·8	8·9	9·0	9·8	9·9	10·0	11·8	11·9	12·0	14·8	14·9	15·0
15·1	58·28	58·93	59·60	64·89	65·5	66·22	78·14	78·79	79·47			
15·2	57·90	58·56	59·21	64·68	65·13	65·95	77·64	78·29	78·96			
15·3	57·71	58·17	58·62	64·04	64·71	65·36	77·13	77·76	78·45			
15·4	57·15	57·80	58·43	63·63	64·28	64·94	76·63	77·27	77·93			
15·5	56·78	57·42	58·06	63·23	63·87	64·52	76·14	76·78	77·43			
15·6	56·41	57·06	57·69	62·82	63·46	64·10	75·65	76·28	76·93			
15·7	56·06	56·69	57·32	62·41	63·05	63·69	75·16	75·78	76·43			
15·8	55·69	56·32	56·96	62·01	62·65	63·28	74·67	75·30	75·97			
15·9	55·35	55·98	56·59	61·63	62·26	62·90	74·22	74·84	75·48			
16·0	55·06	55·63	56·24	61·25	61·87	62·50	73·75	74·37	75·01			
16·1	54·67	55·29	55·90	60·87	61·49	62·12	73·30	73·91	74·54			
16·2	54·33	54·99	55·55	60·49	61·10	61·73	72·85	73·45	74·08			
16·3	53·99	54·61	55·2[illegible]	60·12	60·73	61·35	72·40	73·00	73·62			
16·4	53·67	54·28	54·88	59·75	60·37	60·98	71·96	72·56	73·18			
16·5	53·33	53·94	54·54	59·38	59·99	60·60	71·52	72·11	72·73			
16·6	53·02	53·62	54·21	59·03	59·64	60·24	71·09	71·68	72·30			
16·7	52·70	53·30	53·89	58·68	59·28	59·88	70·66	71·25	71·86			
16·8	52·38	52·98	53·57	58·33	58·92	59·53	70·25	70·81	71·44			
16·9	52·07	52·66	53·25	57·98	58·55	59·17	69·72	70·41	71·01			
17·0	51·77	52·36	52·94	57·65	58·24	58·83	69·42	70·00	70·60			
17·1	51·46	52·05	52·62	57·31	57·89	58·48	69·01	69·58	70·18			
17·2	51·17	51·75	52·32	56·98	57·55	58·15	68·61	69·18	69·77	86·06	86·64	87·22
17·3	50·88	51·45	52·02	56·65	57·23	57·81	68·22	68·79	69·37	85·57	86·14	86·72
17·4	50·58	51·16	51·72	56·32	56·90	57·48	67·82	68·39	68·98	85·07	85·65	86·22
17·5	50·29	50·87	51·42	56·01	56·57	57·15	67·44	68·00	68·58	84·59	85·15	85·72
17·6	50·05	50·58	51·23	55·68	56·24	56·82	67·05	67·61	68·19	84·10	84·67	85·23
17·7	49·72	50·28	50·84	55·37	55·93	56·49	66·67	67·22	67·79	83·62	84·18	84·74
17·8	49·44	50·00	50·56	55·05	55·62	56·18	66·30	66·84	67·42	83·16	83·71	84·28
17·9	49·16	49·72	50·27	54·74	55·30	55·86	65·92	66·46	67·04	82·68	83·24	83·79
18·0	48·89	46·44	49·89	54·44	54·99	55·55	65·55	66·10	66·67	82·22	82·77	83·33
18·1	48·62	49·17	49·72	54·14	54·69	55·25	65·19	65·73	66·30	81·77	82·31	82·87
18·2	48·35	48·90	49·44	53·84	54·39	54·94	64·83	65·37	65·94	81·32	81·87	82·41
18·3	48·08	48·63	49·17	53·55	54·09	54·64	64·48	65·01	65·57	80·87	81·41	81·96
18·4	47·83	48·38	48·91	53·26	53·86	54·36	64·13	64·68	65·22	80·44	80·97	81·53
18·5	47·56	48·10	48·64	52·97	53·51	54·05	63·78	64·31	64·86	80·00	80·54	81·08
18·6	47·32	47·85	48·39	52·69	53·22	53·76	63·45	63·97	64·52	79·58	80·11	80·66
18·7	47·07	47·60	48·12	52·41	52·94	53·48	63·11	63·63	64·18	79·16	79·69	80·23
18·8	46·80	47·34	47·86	52·12	52·65	53·19	62·76	63·28	63·83	78·78	79·25	79·79
18·9	46·50	47·09	47·61	51·84	52·37	52·90	62·43	62·95	63·49	78·30	78·83	79·36

Ten tons of the sulphate of ammonia used would therefore give 41 tons of the compound manure. It would thus be necessary to use 31 tons of potash salt plus superphosphate, or 8·4 tons of the

first and 22·6 of the second. These mixed manures find an outlet chiefly in regions where the vine, tobacco, the hop, and vegetables for preserves are cultivated. They are likewise esteemed for the culture of the sugar beet, barley, and potatoes. Mixtures of superphosphate and potash salts become readily moist in the store, for which reason it is not safe to prepare them a long time in advance. The use of calcined salts prepared from the waste of potash factories suffer from the drawback that they nearly always contain magnesium chloride. When they are dried with precaution at 100° C. they are exempt from basic magnesium compounds. The retrogradation of the soluble phosphoric acid in mixed manures under the action of the basic salts has been studied by Kimmerling following results of culture experiments thereon. By treating salts of potash in the reverberatory furnace to partial fusion, about 800° C. (1472° F.), the magnesium chloride which they contain is decomposed in the moist condition as follows:

$$MgCl_2 + H_2O = MgOHCl + HCl$$

according to the equation—

$$CaH_4(PO_4)_2 + MgO = CaMgH_2(PO_4)_2 + H_2O,$$

a molecule of magnesia as $Mg(OH)_2$, $MgOHCl$, or $MgCl_2$, acts like MgO and may cause the retrogradation of a molecule of phosphoric acid, from which it follows that one part of MgO can render 3·55 parts of phosphoric acid insoluble. If one use, for example, twenty-nine parts of potash salts with 2·05 per cent of free magnesia, the $\frac{2{\cdot}05 \times 29}{100} = 0{\cdot}59$ part MgO suffices to combine $0{\cdot}59 \times 3{\cdot}55 = 2{\cdot}09$ parts of phosphoric acid; but as an actual fact, only 1·4 of insoluble was obtained, which proves that the magnesia did not exert its full action. The cause is to be traced to the slight solubility of magnesia, and in the fact that the salts of potash combine partially with the precipitate formed, so that a part of the phosphoric acid of this latter remains in solution.

Nitrated Phosphate.—The use of nitrate of soda in compound manures is rather restricted; it is used in making nitrated phosphate, sometimes in nitrated phosphate of ammonia. It is found that nitrate of soda and sulphate of ammonia are incompatible and that in fact it is better to use these manures separately. Besides, mixtures of superphosphate and nitrate sometimes enter into spontaneous combustion in the bags. When manure containing nitrate takes fire spontaneously in the bags, however, it is not a case of damp or wet superphosphate, nor is it a case of impure nitrate; but it is due wholly and solely to the superphosphate fresh from the mixing "den" being mixed with the nitrate and bagged up before it has had time to cool. Cold superphosphate,

however damp, does not act on nitrate of soda, except in every warm weather. The superphosphate and nitrate must be mixed dry. They are no longer a source of trouble to the manufacturer, provided that the superphosphate used has been properly made, for dry nitrate of high percentage mixed with a superphosphate, likewise dry, does not give off nitric acid and cause loss of nitrogen as was often the case formerly when superphosphates were wet and the nitrates charged with chloride of sodium. The sodium chloride decomposed by the free phosphoric acid caused the bags to burst in transit, for no substance rots bags so quickly as free chlorine and fluorine, two elements given off when nitrate and damp superphosphates are mixed.

Finally, a manure is made for meadows by mixing kainit with superphosphate or with basic slag. Kainit long in stock is generally so damp that it blocks and chokes up the crusher. The only way to grind it is by hand labour, by the aid of wooden mallets with long arms, and it is altogether a costly operation. Kainit should not be stored in sacks but in bulk on a concrete floor where the water can drain away from it. The mixing entails no difficulty. The ingredients are mixed with a shovel, then the heap is turned over, the product perhaps passed immediately to the centrifugal crusher, then to the sifting machine. If the kainit be in blocks or lumps it must first be put through the crusher to reduce it to the desired fineness.

It has already been remarked that in the case of the ammoniated superphosphate of high strength, the phosphoric acid soluble in water did not retrograde even when the superphosphate entering into the mixture was of such a nature as to readily lend itself to retrogradation. The causes of this phenomenon are of both a physical and chemical nature. The more the superphosphate is distended by ballast, which is here sulphate of ammonia, the more distant the particles are from one another and preserve their condition. From a chemical point of view, sulphate of ammonia possesses the property of hindering the basic sesquioxides from precipitating themselves, but it is clear that a retrograded superphosphate cannot be improved by mixture with sulphate of ammonia.

Tables for the Calculation of Ammoniated Superphosphates.—The first vertical column of Table XLVI gives the content of sulphate of ammonia in per cents of nitrogen, in one-tenths within the limits which are generally met with in practice. The first horizontal column contains the usual percentages in nitrogen of ammoniated superphosphates from 1·85 to 5·00. The figures contained at the points of intersection of these vertical and horizontal columns show the number of cwts. of sulphate of ammonia that must be added to the heaps to get 100 cwts. of the mixture

with the desired nitrogen content. Thus, for example, to get a superphosphate of 5 : 10, with 4·9 per cent of nitrogen from a sulphate of ammonia, of 20·2 per cent of nitrogen, it is necessary to add for 100 cwts. of mixture, say 64 cwts. of a 15·7 per cent superphosphate, 11¾ of some inert material, and 24¼ cwts. of sulphate of ammonia. Table XLV gives the corresponding values for calculating the superphosphates.

TABLE XLVI.—SHOWING IN CWTS. THE AMOUNT OF SULPHATE OF AMMONIA OF DIFFERENT STRENGTHS THAT MUST BE CONTAINED IN A 5 TON HEAP TO GET A MANURE CONTAINING FROM 1·85 TO 5 PER CENT NITROGEN.

Per cent N.	1·85	1·90	1·95	2·00	2·85	2·90	2·95	3·0
19·5	9·49	9·74	10·00	10·26	14·62	14·87	15·13	15·38
19·6	9·44	9·69	9·95	10·21	14·54	14·79	15·05	15·31
19·7	9·40	9·65	9·90	10·15	14·46	14·72	14·97	15·[illegible]3
19·8	9·34	9·69	9·85	10·10	14·39	14·64	14·89	15·15
19·9	9·30	9·55	9·80	10·05	14·32	14·57	14·82	15·08
20·0	9·25	9·50	9·75	10·00	14·25	14·50	14·75	15·00
20·1	9·20	9·45	9·70	9·95	14·18	14·43	14·68	14·92
20·2	9·16	9·41	9·65	9·90	14·10	14·35	14·60	14·85
20·3	9·11	9·36	9·61	9·89	14·04	14·29	14·53	14·78
20·4	9·67	9·30	9·56	9·80	13·97	14·22	14·46	14·71
20·5	9·02	9·27	9·51	9·75	13·90	14·15	14·42	14·63
20·6	8·98	9·22	9·47	9·71	13·83	14·08	14·32	14·56
20·7	8·94	9·18	9·42	9·66	13·77	14·01	14·25	14·50
Per cent N.	3·85	3·90	3·95	4·0	4·85	4·90	4·95	5·00
19·5	19·74	20·00	20·26	20·51	24·87	25·13	25·39	25·64
19·6	19·64	19·90	20·15	20·41	24·74	25·00	25·25	25·51
19·7	19·54	19·80	20·04	20·31	24·61	24·87	25·13	25·38
19·8	19·45	19·70	19·95	20·20	24·49	24·75	25·00	25·25
19·9	19·35	19·60	19·85	20·10	24·36	24·62	24·87	25·13
20·0	19·25	19·50	19·75	20·[illegible]0	24·25	24·[illegible]0	24·75	25·00
20·1	19·15	19·40	19·65	19·90	24·13	24·38	24·62	24·88
20·2	19·05	19·31	19·55	19·80	24·01	24·25	24·50	24·75
20·3	18·97	19·22	19·45	19·71	23·89	24·14	24·39	24·63
20·4	18·88	19·12	19·30	19·61	23·78	24·02	24·27	24·51
20·5	18·78	19·02	19·27	19·51	23·65	23·90	24·14	24·39
20·6	18·69	18·93	19·17	19·42	23·54	23·79	24·03	24·28
20·7	18·60	18·84	19·08	19·32	23·43	23·67	23·91	24·15

CHAPTER IX.

THE MANUFACTURE OF PHOSPHORIC ACID, DOUBLE SUPERPHOSPHATES, AND VARIOUS PRODUCTS.

Historical Review.—The manufacture of phosphoric acid, at one time flourishing, has lost much of its former importance. The market for raw materials and finished products constitutes one of the most important factors in the development in this as of any industry. Formerly, when pure phosphates of high strength were rare, whilst phosphates of low strength abounded, the phosphoric acid industry and the preparation of its derivatives were in an excellent and prosperous condition. The extensive deposits of phosphorite in Germany induced manufacturers to devote themselves to the manufacture of a product which, after separation from the impurities accompanying it in the raw material, was admirably adapted for the manufacture of one of the most esteemed manures, that is, the double superphosphate. The discovery of the Lahn phosphorite beds occurred about the same time as that of the Strassfurt deposits of potash salts, and just when Liebig had formulated his mineral manure theory. Lahn phosphorite, which, we know, contains a large proportion of iron and alumina, was received with open hands by manufacturers, but great was their astonishment when they realized that this material was absolutely unfit for superphosphate manufacture. Treated with sulphuric acid, it yielded a product, with a very low content of soluble phosphoric acid, which diminished still further to such an extent owing to retrogradation that superphosphate manufacturers had to abandon its use. Two large chemical factories, which owned a great part of the Lahn phosphorite deposits, subsequently endeavoured to utilize the material in phosphoric acid manufacture.

The fundamental idea of the process of manufacture is contained in Graham's method of analysis. It consists in digesting the pulverized phosphate with sulphuric acid of 5 per cent strength, the dissolved phosphoric acid being afterwards titrated with uranium solution, leaving the oxide of iron intact. The principle of the process is thus represented by the following equation :—

$$\underbrace{\underset{310}{Ca_3(PO_4)_2} + \underset{294}{3H_2SO_4}}_{604} = \underbrace{\underset{408}{3CaSO_4} + \underset{196}{2H_3PO_4}}_{604}$$

By some strange error the older manuals state that by treating tricalcic phosphate with dilute sulphuric acid, monocalcic phosphate is obtained. Now this statement is erroneous because, as will be seen later, only phosphoric acid enters into solution. But even when sulphuric in insufficient amount to that calculated for the preparation of monocalcic phosphate is used, free phosphoric acid is obtained, seeing that in this case a part of the $Ca_3(PO_4)_2$ remains undecomposed. As far back as 1870, the firm of H. & E. Albrecht at Biebrich installed an experimental factory for the manufacture of phosphoric acid, but the venture was not successful because at that time suitable appliances for separating the phosphoric acid from its insoluble residue were not then utilized. It was only by the use of the filter press, already known at that time in sugar works, that the manufacture of phosphoric acid became lucrative, but the conversion of dilute phosphoric acid into double superphosphates did not in the beginning present insurmountable difficulties. Now, for this double superphosphate—with a minimum of 40 per cent P_2O_5—there was soon a very great demand, as much by agriculturists as by manure manufacturers, to whom it afforded a simple and easy means of securing a high percentage of P_2O_5. But let us examine the manufacture of phosphoric acid a little more closely.

Manufacture of Phosphoric Acid.—The raw material used is a 50 per cent phosphate ($Ca_3P_2O_8$). If damp, it is dried on metal plates. If lumpy the lumps are crushed by a stone breaker and then reduced to the requisite fineness by a flatstone mill or a ball mill. The ground phosphate is then fed into the vats by a chain elevator, 1 to 2 tons per charge; the sulphuric acid and the necessary water (wash water containing some P_2O_5) to dilute the acid to 16° B. is run in at the same time. The charging of the vats requires twenty minutes, and during this time decomposition is completely effected, the phosphoric acid being liberated, the sulphuric acid has taken its place and combined with the lime to form gypsum, which has to be separated from the liquid. For this purpose the muddy liquids from the decomposition vats are collected in a receiving tank at a lower level; this is fitted with an agitator, its rôle being to maintain the solid particles in suspension until the mixture is forced to the filter presses by a pump, in which the acid liquid comes in contact only with rubber or lead. The filter presses used have 50 plates, and are capable of treating 14 tons of phosphate—equal to three tons of P_2O_5—in twenty-four hours. The filter plates are of pitchpine, the frames being of the same wood or of oak. The gutters are of plum-tree wood. When the filter press is charged, its contents are washed with water under pressure until the liquid which flows away shows a gravity of only 0·25° B., a density equal to that of gypsum-saturated water. The wash water then contains on

an average 3 per cent of P_2O_5; it is used, as already stated, to reduce the sulphuric acid to 16° B. The phosphoric acid collected in a "weak solution" tank has a density of about 12° B., say about 4° B. less than the sulphuric acid used; there is reason to conclude that in addition to liberating the phosphoric acid a part of the latter has combined with the lime present in the phosphate as $CaCO_3$, CaF_2, and $CaSiO_3$. A weak phosphoric acid solution of average quality has the following composition:—

	Per cent.
P_2O_5	8·0
SO_3	0·2
CaO	0·4
Fe_2O_3 and Al_2O_3	0·3

and small quantities of HF, Si, MgO, etc. For most applications, especially for the manufacture of double superphosphates, the phosphoric acid must be concentrated to a certain extent. At first attempts were made to concentrate it by evaporation, using lead steam coils, but the pipes became rapidly encrusted with lead salts and lost their conductivity for heat. This process was therefore abandoned, and attempts made to concentrate the acid by bottom heat. Great flame ovens were constructed heated by combustion gases. These gases are led underneath the liquid contained in a pan surmounted by an arch. The pan is of strong wrought-iron, lined inside with stones which resist acid, and thus was protected from direct contact with the flame and the phosphoric acid. On the other hand, the exterior side of the pan is unprotected. The dilute solution of phosphoric acid runs in continuously in the back part of the pan, until after two or three days an average concentration of 50° B. is obtained. The concentration is then finished and the phosphoric acid, now indicating 56° to 58° B., is finally run out by a central gutter, whilst the contents of the pan are continuously agitated so that no mud remains. The liquid is collected in wooden vats, or in lead-lined iron tanks. In this condition the phosphoric acid is turbid and blackish owing to the presence of soot deposited by the combustion gases. It contains about 54 per cent P_2O_5, 1·5 per cent of Fe_2O_3 and Al_2O_3, and variable amounts of gypsum, phosphate of lime, calcium fluoride, hydro-fluosilicic acid, arsenic, etc.

Up to 1890, the factory of H. & E. Albrecht treated about 60 tons of phosphate in twenty-four hours. Five large evaporation ovens, analogous to those described, were installed, which evaporated the enormous amount of 200 tons of water in twenty-four hours. The largest of these evaporating pans was 16·5 metres (50 feet) long, and 5·5 metres (17 feet) wide, but it was divided into two compartments by a longitudinal diaphragm. It had a capacity of

36 cubic metres, and yielded at one operation 55·8 tons of 54 per cent phosphoric acid, vaporizing 270 tons of water with an expenditure of 35 tons of coal, 100 kg. (220 lb.) of coal vaporized, 770 litres (1694 lb.) of water (i.e. 1 lb. of coal furnished nearly 8 lb. of steam), and yielded 160 kg. (352 lb.) of concentrated phosphoric acid. The evaporation was at the rate of 1626 litres (32 cwt.) per hour.

The ovens installed at the Wetzlar factory were not so large. When the acid was brought to the desired density it sometimes happened, owing to want of supervision, that in the parts of the pan most exposed to the heat the phosphoric acid was evaporated to dryness, and vitreous lumps of a greyish-blue colour, partially diaphanous, formed. The analysis of this vitreous mass was very difficult, because it was impossible to dissolve it by ordinary methods. Prof. Krantt, of Hanover, however, succeeded in dissolving it, by heating it with borax; the analysis gave 70 per cent of P_2O_5, besides alumina, iron, lime, alkali, and hydrofluoric acid; silica, supposed to be present in large amount, judging from the vitreous nature of the mass, was only found in traces combined with fluorine. The substance thus consisted chiefly of metaphosphoric acid. In the evaporation of the phosphoric acid, the steam carries off a great part of the dissolved HF and H_2SiF_6.

Manufacture of Double Superphosphate.—The greater part of the phosphoric acid so produced was used in the manufacture of double superphosphates. This manufacture is distinguished from ordinary superphosphate manufacture by the fact that phosphoric acid is substituted for the sulphuric acid. The phosphate is then rendered soluble according to the following equation:—

$$\underbrace{\underset{310}{Ca_3(PO_4)_2} + \underset{392}{4H_3PO_4}}_{702} = \underbrace{3CaH_4(PO_4)_2}_{702}$$

It is clear that in actual practice the method of conversion is not so simple, because phosphates containing all manner of impurities are used, and the nature of the phosphoric acid, as well as that of the superphosphate, plays a preponderant rôle. The phosphates which are the most easily dissolved by phosphoric acid, are sandy phosphates with a high percentage of carbonate of lime, such as Somme phosphate and Malogne phosphate. This phosphate is mixed in the proportion of 1 ton to 4 tons of 54 per cent phosphoric acid. This mixing is done in the same manner, and with the plant, as that in which the phosphate is dissolved by sulphuric acid. To elevate the concentrated phosphoric acid and bring it to the mixing apparatus, either a force pump, a centrifugal pump, or an injector is used. The first of these pumps is sure in its working

and can elevate the acid to any desired height; the second, which lends itself more particularly to the elevation of dilute phosphoric acid, is liable to stop working when the acid is concentrated or muddy; injectors are the most convenient, but it must be remembered that they dilute the acid 1° to 2° B. The ordinary appliances for raising sulphuric acid in manure works can, however, be used, viz. the ordinary "montejus," sometimes called the egg or air vessel. This air vessel is filled with acid by a syphon from a tank alongside. When full, air is pumped into it by one pipe and the acid rises from it up another pipe into the ten ton store tank overhead. Any hitch with the pumps described by the author means, of course, the stoppage of the mixing when the store tank is empty. The air vessel with ordinary attention gives no trouble.

The principal difference which exists between double superphosphate and ordinary superphosphate lies in the fact that the latter is a mixture of monocalcic phosphate and gypsum, whilst double superphosphate only contains as impurities a very small amount of gypsum, forming essentially a monocalcic phosphate containing free phosphoric acid in excess. That is why double superphosphate is less easily dried than ordinary superphosphate, and must therefore be very carefully dried by artificial means.

The process of manufacture just described appears very simple; it none the less requires the control of a good chemist, the more so as the raw material used is always contaminated with impurities. The following example will show what field of action is here open to the chemist. Wetzlar's factory, of which the daily production of double superphosphate was about 12 tons, made a product in 1883 containing 34 per cent P_2O_5 soluble in water and 13 per cent P_2O_5 insoluble in water; two years afterwards the P_2O_5 soluble in water had risen as high as 43 to 45 per cent with 3·6 insoluble in water. 100 kg. of phosphoric acid in the merchandise consisted therefore—

In 1883 of the total of phosphoric acid 73·2 kilos soluble in water.

In 1885 the phosphoric acid soluble in water was increased to 90·8 kilos.

As at that time phosphoric acid soluble in water was valued at 0·65 franc the kg., whilst insoluble in acid was not generally paid for at all, the above improvement represents an increase in profit of £25 per day without taking into account the other advantages attached to the improvement in the working. The capital point in the manufacture of phosphoric acid is to dissolve the least possible amount of sesquioxide (Fe_2O_3 and Al_2O_3), because it is to their presence in superphosphate that its retrogradation is due. It is clear also that the phosphates ought to be exhausted as completely as possible to reduce the expenditure of sulphuric acid to the minimum and to leave the least amount of impurities, lime, hydrofluoric

acid, etc., in the weak solutions. Up to 1884, it was believed that the longer the action was prolonged in the mixing tank, the more complete was the extraction of the phosphoric acid. It was further believed that a temperature of 60° to 80° C. or 140° C. (176° F.) was necessary, or was at least conducive to the progress of the operation. Thus the acid and the water were mixed in the mixing vat, the heat of the reaction bringing the temperature of the mixture to 70° C. (158° F.); the phosphate was then run in and the agitator was kept moving for two to three hours. But this was not a good method of working. Systematic manufacturing tests have led to the following conclusions:—

1. The percentage of sesquioxides in the weak solution increases with the period of the agitation and with the rise of temperature, the other impurities HF, H_2SiF_6, CaO, behaving in the same way.

2. The percentage of phosphoric acid in the insoluble residue is least when the agitation lasts not longer than twenty minutes, from that time onwards it decreases with the duration of the agitation, but in proportion to the oxide of iron content. There would appear to be a retrogradation of the free phosphoric acid, under the influence of the oxide of iron, as in superphosphates.

3. The expenditure of sulphuric acid increases with the duration of the agitation and the elevation of the temperature. Under opposite conditions, the sulphuric content of the "weak solutions" naturally decreases. These deductions were arrived at in the course of manufacture from Lahn phosphorite; afterwards they were generalized, especially for verifying the facts pointed out in 1 and 3, which are likewise applicable to Liége phosphate. The results thus ascertained were applied immediately in industrial practice. To diminish the duration of the mixing process was easily done; to lower the temperature of the mixing during working, the sulphuric acid was diluted with the wash water and the hot dilute acid passed through a tubular condenser, cooled by a circulation of water; finally, to decompose the phosphate by sulphuric acid, half quantities were taken. Great advantage arises from this method of working, less handling, abolition of night work by installing of new filter presses, economy of sulphuric acid, more complete extraction of the phosphoric acid from the phosphates, longer life of the filter cloths, and above all, obtaining a product richer in phosphoric acid soluble in water. This product then had the following composition:—

TABLE XLVII.—SHOWING THE ANALYSIS OF DOUBLE SUPERPHOSPHATE.

	Per cent.	
Monocalcic phosphate $CaH_4(PO_4)_2$	60·0	
Free phosphoric acid H_3PO_4	9·5	
Dicalcic phosphate $Ca_2H_2(PO_4)_2$	4·5	
Tribasic phosphate $C_3(PO_4)_2$	2·0	48·1 per cent of total P_2O_5.
Phosphates of iron and alumina $FePO_4AlPO_4$	4·0	43·3 per cent of P_2O_5 soluble in water.
Hydrated sulphate of lime $CaSO_42H_2O$	5·0	
Magnesia, silica, fluorine	2·0	
Sand, etc.	4·0	
Moisture	9·0	
	100·0	

But all the manufacturing problems were not solved. An important point is the exact determination of the amount of sulphuric acid required to decompose the phosphate. That amount cannot be fixed, except by inference from the SO_3 in the weak solution of a preceding operation, and to determine that it is necessary to make a quantitative analysis. If a sufficient amount of acid be not used the solution contains lime in excess, and after evaporation it is often converted into a thick liquid, which it is impossible to work in that condition. This drawback is remedied by introducing more sulphuric acid, but it would be better not to use that expedient owing to the disengagement of hydrofluoric acid fumes. Another drawback which arises from a deficiency of sulphuric acid, is that the extraction of the phosphoric acid is incomplete. But an excess of sulphuric acid causes even greater drawbacks. In fact, if the phosphoric acid solution, with excess of sulphuric acid, be evaporated, it becomes inactive towards the phosphate which it is intended to dissolve, which is likewise the case with too concentrated sulphuric acid. The phosphate is in this case not attacked by the acid, and the manufacturer is in a dilemma as to what to do with this dilute mixture of phosphate and phosphoric acid. At the Wetzlar factory, when this mishap occurred, the phosphoric acid was absorbed by powdered peat, in the ratio of three to one; this product contained about 33 per cent of P_2O_5, and when it could not be sold directly, it was afterwards mixed with double superphosphate. When finished, the percentage of phosphoric acid soluble in water was thus considerably increased, but at the expense of its physical properties.

Afterwards, a very simple way was found to restore the activity to phosphoric acid which had become inactive. All that has to be done is to treat it with finely powdered quicklime. But phos-

phoric acid so treated does not behave like normal acid in the course of the work. As already stated, the residual gypsum left in the filter presses forms a very cumbersome waste product. It contains 40 to 50 per cent of water. It is run on to a heap. In summer it dries on the surface, it is then turned over with the plough, and passed through a Carr's disintegrator, and marketed as a powder. In wet years it is dried in a simple drying machine, when there is an outlet for it. This product is known in commerce as phosphatic gypsum; it contains 60 per cent of gypsum and 3 to 4 per cent of phosphoric acid, of which 1 per cent is soluble in citrate and 0·25 soluble in water. It appeared that this gypsum could be specially adapted as a preservative agent of the fertilizing principles of farmyard manure, for which purpose it has been proposed to spread it in stables and on farmyard manure. This use is very rational, for precipitated gypsum reacts very readily with the ammonium carbonate of farmyard dung. But it is clear that this material cannot bear heavy freight charges, since its selling price is almost entirely absorbed by drying expenses and loading. It is easy to understand that to a factory which produces 100 tons of phosphatic gypsum a day, the sale of this waste is of no great importance in itself, whilst the handling of it and its storage form a big item in the general expenses account. Thus the Wetzlar factory was obliged to purchase a piece of land for 30,000 marks (£1500) for this purpose and to instal on it an aerial conveyer at a cost of 16,000 marks (£800).

It has already been seen that double superphosphate must be dried artificially. The principle of this operation consists in passing over the substance a large volume of air at a uniform temperature, the degree of which depends on the superphosphate. The dryers installed at first fulfilled none of these conditions; the product obtained therefore was very unequal, one part being superheated and its phosphoric acid partially retrograded. To improve the drying plant experiments were undertaken to find the limit of temperature at which the phosphoric acid ceased to retrograde. These researches were made on Lahn double superphosphate and gave quite unexpected results. Up to 120° C. (248° F.) the content of phosphoric acid soluble in water underwent no modification, it even appreciably increased between 120° C. (248° F.) and 170° C. (338° F.), and it is only above 170° C. that the objectionable retrogradation occurred. At first sight one would be inclined to explain this fact by inferring that the H_3PO_4 and $Ca_2H_2(PO_4)_2$ are at a low temperature in a state of equilibrium in superphosphate, but react one on the other at a high temperature to form $CaH_4(PO_4)_2$. It was then a question of realizing this temperature of 170° C. in actual practice. But this problem is a difficult one and does not appear to have ever been perfectly solved. It will be seen in the sequel that double super-

phosphate made from Liége phosphate behaves in quite a different manner; not only is there no increase in the phosphoric acid soluble in water, but retrogradation commences as soon as the drying temperature exceeds 120° C. The true cause of that difference in the behaviour of the two superphosphates has not been ascertained, but it may be concluded that each phosphate has distinct properties of its own, and requires to be treated in accordance therewith. It is the phosphates poor in sesquioxides which work best, such as Florida phosphate which is used in a Swedish factory. The crushing of the dried superphosphate is done in a Carr's disintegrator, like an ordinary superphosphate, and presents no difficulty. The plant required for making 7½ tons of 55 per cent phosphoric acid is the following:—

4 to 5 filter presses.
1 large and 3 small mixing vats.
2 centrifugal pumps.
3 force pumps.
Cooling and dilution plant.
Sulphuric acid store tank, 10 cubic metres capacity.
35-40 per cent sulphuric acid store tank, 20 cubic metres capacity.
2 sulphuric acid measuring tanks.
2 wash water tanks, 15 cubic metres capacity.
Dilute phosphoric acid tank, 40 cubic metres capacity.
Concentrated phosphoric acid tank, 10 cubic metres capacity.
Force pump for concentrated phosphoric acid.
Oven for drying the phosphoric acid.
Lead piping.
1 steam engine 25 H.P. with shafting.

As mentioned at the outset, the phosphoric acid industry has lost much of its importance. Of twelve large factories at work twenty years ago, there are only four or five still at work, which also make various kinds of phosphates, of which a few words will now be said.

Manufacture of Superphosphate of Potassium and Ammonium.—The oldest and the most important of the phosphoric acid derivatives is the neutral phosphate of sodium, Na_2HPO_4, which occurs in the form of beautiful monoclinic crystals consisting of 20 per cent Na_2O, 20 per cent P_2O_5, and 60 per cent of water, and can therefore be prepared easily in the pure state. The phosphate of sodium is not employed as manure, but rather the phosphate of potash and of ammonia about to be described. The manufacture of phosphates of potassium and ammonium presents difficulties, especially that of potassium, owing to its weak crystallizing power. From that point of view, the mono-ammonium phosphate $NH_4H_2PO_4$, which is the most stable of all the phosphates of ammonia, behaves much better.

It crystallizes without water of crystallization in beautiful tetragonal prisms with a pointed apex. The acid phosphates are generally very difficult to filter when they are neutralized with soda. Now as the pure non-ammoniacal phosphate is much less used as a manure than the impure phosphate of ammonia, the manufacture of the latter furnishes a pure ammoniacal salt as a secondary product. The most simple process to manufacture phosphate of ammonia, as well as sulphate of ammonia, is to use gas liquor, working with the well-known apparatus of Feldmann. The salt is not separated from the muddy precipitate obtained, which is likewise used as manure, but there forms at the surface fine crystalline efflorescences of $NH_4H_2PO_4$, which it is easy to collect apart and to purify by fresh crystallization. In order to prepare in the same manner a crude phospho-potassic manure, potash must be employed as the raw material, but that is too dear. Nevertheless, in 1892, the Biebrich factory produced small quantities of phosphate of potash, by saturation of potash with phosphoric acid, although the product was of bad quality (much insoluble P_2O_5 and H_2O).

Manufacture of Sulpho-phosphates.—During this period chemists tried new methods of manufacture. At that time Dr. Paul Wagner, 1892, published his pamphlet on the use of chemical manures in horticulture, suggesting the manufacture of pure and concentrated chemical manures. This idea was taken up by H. Albrecht, director of the Biebrich factory, which henceforth manufactured phosphates of potash and ammonia and nitrate by mixing the ingredients in different proportions. As a matter of fact, an impure phosphate of potash was known as early as 1886, but its content of sulphuric acid rendered it unfit for the purposes to which such mixtures are applied. This product is the sulpho-phosphate of potash which was at first made by Meyer, as well as an analogous product, the sulpho-phosphate of ammonia.

The sulpho-phosphates are interesting from several points of view, and possess such valuable properties that there is reason to inquire why agriculture and the chemical manure trade do not make more frequent use of them. So long as the Wetzlar factory was at work, it produced great quantities intended chiefly for export to the Dutch East Indies, but from that time they have not been heard of. If equal parts of 55 per cent phosphoric acid and of sulphate of ammonia or sulphate of potash be mixed together and heated to 80° C., the components unite to form a dry pulverulent salt, an additive product of the two substances being formed :—

$$(NH_4)_2SO_4 + H_3PO_4 = NH_4HSO_4 + NH_4H_2PO_4$$
$$K_2SO_4 + H_3PO_4 = KHSO_4 + KH_2PO_4$$

The products contain respectively, 25 per cent P_2O_5 and 10·5 N, and 24 per cent P_2O_5 and 27 K_2O. The phosphoric acid is present

in a condition almost entirely soluble in water. The percentage of sulphuric acid is about 30 per cent. (It may be remarked as peculiar that an analogous compound cannot be obtained from soda in this way.) The manufacture is exceedingly simple. There is dissolved in the "weak solution," obtained in the manufacture of phosphoric acid, an equivalent quantity of alkaline sulphate, viz. 100 $(NH_4)_2SO_4$ for 55 P_2O_5 and 100 K_2SO_4 for 48 P_2O_5, and the solution is evaporated until the boiling-point rises to 110° C. (230° F.) for the potash salt and 140° C. (284° F.) for the ammonia salt. Finally, the hot mass is run into a cooling beck and agitated until it solidifies. This process is much more simple and cheaper than that of making double superphosphate. It is well to take into account the advantages which the sulpho-phosphate possesses in virtue of its acid nature. It may be used in large quantities in calcareous and heavy soils, either alone or mixed with basic slag or powdered lime. We know that in virtue of its high lime content, basic slag cannot be mixed either with ammoniacal salts nor with superphosphates, for in the first instance there would be a loss of nitrogen, and in the second of phosphoric acid soluble in water. Now, not only does the mixture of basic slag with the sulpho-phosphate of ammonia exclude losses of this nature, but it also has the effect of increasing the percentage of phosphoric acid soluble in water. According to experiments made on this subject this increase reached 13 per cent of the total phosphoric acid in the mixture. Another advantage arising from the acid character of the sulpho-phosphates resides in the possibility of using particularly impure phosphates such as those containing oxide of iron and alumina. It is precisely this fact which will bring the sulpho-phosphates into good repute some day, when the abundance of pure phosphates has become a thing of the past.

But there is a class of mineral phosphates of low content in lime, and the base of which is alumina with more or less oxide of iron. Redonda phosphate consists of important beds of this nature. These phosphates cannot be treated either by the ordinary dissolving process or by the process of extraction of the phosphoric acid, because the latter is present in a form difficult of attack. Now the manufacture of sulpho-phosphates presents us with the means of profiting excellently by these phosphates which are otherwise unutilizable, and therefore cheap. The method about to be described, and which has not previously been published, is based on the following equation:—

$$2AlPO_4 + 4NH_4HSO_4 + H_2SO_4 =$$
$$Al_2(SO_4)_3 + 2(NH_4HSO_4.NH_4H_2PO_4)$$

The ground phosphate is fused at a temperature of 120° to 140° C. with super acid ammonium bisulphate. The duration of this

operation depends on the degree of resistance of the substance. Most often it requires two to three hours. It is clear that the water evaporated in that time must be replaced. The phosphate is dissolved much more rapidly and more completely when the operation is performed under pressure and at an elevated temperature. The plant required by this method of working is certainly more costly, but the work would be more expeditiously done and factory expenses consequently less.

The product so obtained is a sulpho-phosphate of ammonia and sulphate of alumina. The presence of the latter renders it very hygrometric and little fitted for its intended use. But there is a very simple method of remedying this drawback. If an equivalent quantity of sulphate be added thereto it combines with the sulphate of alumina to form a double sulphate of alumina and ammonia (alum). A product is thus obtained which remains as dry as ordinary phosphate. The chemical transformation then becomes :—

$$AlPO_4 + 3NH_4HSO_4 = AlNH_4(SO_4)_2 + NH_4HSO_4,NH_4H_2PO_4$$

If the Redonda phosphate contains, for example, 40 per cent P_2O_5, one calculates thus :—

100 phosphate	$40P_2O_5$
112 sulphate of ammonia	$24N$
130 sulphuric acid of 50 B.	$8IH_2SO_4$
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We thus get a manure containing in round figures :—

	Per cent.
Nitrogen	8·0
P_2O_5 total	13·0
P_2O_5 soluble in water	11·0

In many cases it would be advisable to replace a portion of the nitrogen by potash. This substitution is easily effected. It suffices to replace the sulphate of ammonia by sulphate of potash :

$$AlPO_4 + 2NH_4HSO_4 + KHSO_4 = AlK(SO_4)_2 + NH_4HSO_4,NH_4H_2PO_4$$

The addition of potash in quantity greater than that required to combine with the alum complicates the work. It is clear, moreover, that one can likewise combine with this process the production of aluminate of potash ; the expense adherent to washing, evaporation, and crystallization appears to be largely covered by the sale of the sulphate of alumina as a current article of commerce, whilst the richness of the manure could be increased at will.

By working as described, it is easy to utilize Redonda phosphate

up to 90 per cent. As already mentioned, the sulpho-phosphate of potassium does not combine the conditions required in a concentrated potassic manure. Its sulphuric acid, amounting to almost 30 per cent, must be removed. Lime provides the easiest means of doing this. It has been proposed to combine monocalcic phosphate with sulphate of potash, but the process is not applicable, because the gypsum is precipitated in the form of very attenuated crystals, which render filtration impossible after evaporation. But if lime in an insoluble form be used, i.e. as carbonate, and if it be made to react on the dissolved sulpho-phosphate of potash, the gypsum is precipitated in a coarse state, and its elimination from the liquid by filtration presents no difficulty. The free sulphuric acid of the sulpho-phosphate combines with the lime to form gypsum; by addition of phosphoric acid, the K_2SO_4 is transformed into $KHSO_4 + KH_2PO_4$, and the acid of this new bisulphate is in its turn removed by $CaCO_3$. The sum of these reactions is represented by the following equation:—

$$K_2SO_4 + 2H_3PO_4 + CaCO_3 = 2KH_2PO_4 + CaSO_4 + CO_2 + H_2O$$

However, these reactions are not effected in the simple manner shown above. Thus the direct action of calcium carbonate on phosphoric acid is to form insoluble phosphate of lime. If it is desired to treat a solution of potassium sulphate in dilute phosphoric acid there would be a considerable loss of phosphoric acid. Moreover, the washing of the precipitated gypsum containing P_2O_5 and the evaporation of the wash water would entail great expense, sufficient perhaps to absorb all the profit of the manufacture. An elegant and simple solution to the problem, however, has been found by the use of grey phosphatic chalks. These phosphates, for which formerly no use could be found in spite of all the researches and tentative trials made, contain about 30 per cent of $Ca_3(PO_4)_2$, and a preponderant quantity of $CaCO_3$; they are sold cheap. It is clear that, if in the process now described, calcium carbonate be added as phosphatic chalk, there will be obtained as a filtration residue a mixture of phosphate and gypsum, the phosphoric acid content of which, although low, can be perhaps utilized for the extraction of phosphoric acid. And if the phosphoric acid extracted from it is afterwards used in the manufacture of sulpho-phosphate of potash, it will suffice to treat the above phosphatic gypsum in the filter press to eliminate the adherent solution of potassic phosphate, but it would be useless to wash it, because the remainder of the potassic phosphate which it contains returns to the process by the extraction of the phosphoric acid. In this way the small amounts of phosphoric acid precipitated by the chalk would also be utilized. This detail also brings out better the advantages resulting from the use of phosphatic chalk in this case; in fact the amount of phos-

phoric acid precipitated is exceedingly small, because the conversion is effected in a less violent and more regular manner. Another very disagreeable drawback due to the carbonate of lime, is obviated by using phosphatic chalk; it is the entrainment of soluble potash by the gypsum sludge, owing either to the formation of a double phosphate of calcium and potassium or to adsorption. The process just enunciated was the subject of a patent delivered to H. & E. Albrecht; it is applied on the large scale at the Biebrich factory, in the manner about to be described.

There is run into a lead-lined vessel, fitted with an agitator, a measured quantity of a 10 per cent solution of phosphoric acid, in which a corresponding quantity of sulphate of potash is dissolved. Afterwards, whilst constantly stirring the mixture, but without heating, the calculated quantity of pulverized phosphatic chalk is slowly incorporated. When, after about an hour, the conversion is accomplished, the phosphatic solution is separated from the residue by filter presses, and the liquor evaporated to a pasty consistency by steam heating. The dry salt is afterwards obtained, fit to be centrifuged by drying it in a special chamber heated by steam at a temperature of 70° to 80° C. From the filter presses, the residue falls directly into a second mixing tank with agitator, likewise lined with lead, and containing the quantity of sulphuric acid necessary to decompose the phosphate. When this decomposition is complete, the residue is separated from the liquid by means of the filter press, completing the extraction this time by washing, for the wash water afterwards serves to dilute the sulphuric acid. The filtrate, which consists of a mixture of phosphoric acid and potassic phosphate, flows from the filter press directly into the first receiver-mixer. The product thus obtained contains 38 to 40 per cent of P_2O_5 almost entirely soluble in water, 31 to 33 per cent of K_2O, and in addition a few per cents of sulphuric acid, lime, etc.

The Salz Werke Co., Neustassfurt, have likewise succeeded in producing a pure and concentrated phosphate of potash from potassium chloride. The experiments made by this company led to quite an unexpected result. It is known that the metaphosphate obtained by the decomposition of potassic chloride, by phosphoric acid, at the temperature of fusion, is by itself completely insoluble in water, and even in acids. Now it has been found that by cooling it suddenly, it is converted into a modification very soluble in water. The decomposition is effected in a muffle furnace for the preparation of phosphate, the evolved hydrochloric acid is condensed, and the liquid metaphosphate flows boiling from the oven direct on to cold plates, in a thin layer. After crushing, the product forms a dry salt easily preserved and containing 50 per cent P_2O_5 and 45 per cent K_2O. Although phosphate of potash, and similar concentrated manures, have not assumed, in agriculture, the importance

that was at first anticipated, especially for cereal cultivation, they have none the less a great importance in certain special cultures, and above all in the Colonies, owing to freight charges, which are heavy. Their rational use in horticulture likewise presents very great advantages which will eventually be appreciated. Here is an example: In the garden attached to the mansion house of Biebrich, in 1892, phosphate and nitrate of potash was applied to the raspberry plantations with the object of obtaining a heavier and an earlier yield. The success was such that the gardener of the mansion house had already sold £15 worth of fruit collected in the squares so treated before the raspberries in the plants cultivated without manure were ripe (end of April). Now the amount of fertilizer used hardly came to the value of 1s.

Bisulphate Superphosphate.—It now remains to say a word about another product not previously described, i.e. the bisulphate superphosphate. Bisulphate, as is well known, is a by-product of the manufacture of nitric acid (nitre cake), and finds hardly any use, except in glass works and in the manufacture of Glauber's salt. But it is difficult to sell, and it is sold at a very low price, for the local authorities forbid it being run into streams. Dr. Grueber tried to utilize it in the manufacture of superphosphates. By mixing 500 kg. of bisulphate with 150 kg. of Algerian phosphate he obtained a superphosphate, but the product was very deliquescent because it wanted the water of constitution necessary to the formation of sulphate of lime. Dr. Grueber remedied that by adding to the phosphate 60 kg. of water. He thus obtained a dry superphosphate, with 7 to 8 per cent. of soluble phosphoric acid; the addition of a small amount of Algerian phosphate enabled it to be passed through the centrifugal crusher and thus it was obtained in a pulverulent form. As all manure factories require poor superphosphates to adjust the analysis, this product would thus readily find a use.

Phosphatic Peat.—It now remains to describe a manure in which the phosphoric acid is present, not in chemical combination but in simple admixture—we mean phosphatic peat. In 1892 the Society of German Agriculturists greatly recommended the manufacture of this product as a microbicide, as a preventative of epidemics, and suitable for rendering both human and animal excreta inoffensive. The first experiments made in this direction with hydrochloric and sulphuric acid did not yield satisfactory results; hydrochloric acid is too volatile, while sulphuric acid carbonizes the fibre of the peat, so that it is difficult to use more than 2 per cent in the mixture. Phosphoric acid has not either drawback, and there is nothing therefore to prevent phosphatic peat being prepared with 10 to 15 per cent of P_2O_5. Experiments on a manufacturing scale, and application of this product, were made

in 1893 by Dr. Meyer, who, moreover, exhibited samples at the show of the German Society of Agriculturists, who made him an award. There is no doubt that phosphatic peat possesses the properties which recommend it, more particularly for spreading on farmyard dung in stables. The excrements of animals commence to decompose as soon as they are evacuated, and this decomposition is accompanied by a considerable loss of nitrogen. The addition of the phosphoric acid not only retains all the nitrogen in the manure, but also enriches it. It also destroys the germs of infectious disease, typhus, cholera, etc., as the experiments of Fraenkel, Klipstein, and Burow have shown. Klipstein formally declares that phosphatic peat behaves better in this way than sulphated peat, which he had prepared with 10 per cent of sulphuric acid. The manufacture of phosphated peat is very simple. The peat is made to absorb the quantity of hot phosphoric acid diluted to the desired strength. Prepared peat or crude peat may be used. In the latter case, the peat should be passed through a slicing machine and then through a press. This industry should be profitable. To obtain the phosphoric acid the most impure phosphates, otherwise of no value, can be used; moreover, the phosphoric acid absorbed by the peat retains its solubility in water. On the other hand, it should not be very difficult to create a market, since peat has been employed for a long time as litter, as well as other additional matter, i.e. gypsum from superphosphates, which is spread in the stables. But there is no substance of this nature which possesses the anti-septic properties of phosphatic peat. It retains the nitrogen, destroys infectious germs, absorbs urine, purifies the air of stables, amplifies and enriches farmyard manure. The use of phosphatic peat for the disinfection of fæcal matter constitutes a problem more difficult to solve. The main obstacle is the system of water carriage that all large towns have adopted to free themselves of their excreta in a radical but far from economical manner. In small towns (there are some in Germany where the use of phosphatic peat is obligatory) its purchase, its use, and the sale of the human manure under the control of the authorities, to prevent fraud, present real difficulties. But on large estates which have the use of the manure in their own hands, the use of phosphatic peat would be very rational in so far as one could then economize the cost of drying. But if it be desired to dry the manure, plant similar to that used for drying poudrette may be used. The manure, consisting of fæcal matter and phosphatic peat, after desiccation forms a manure analogous to guano. It does not give off any bad odour, and contains 4 per cent of N, 4·5 per cent P_2O_5 ($\frac{4}{5}$ soluble), 1 per cent potash, and about 45 per cent of peat.

APPENDIX.

THE MANUFACTURE OF PHOSPHORUS IN THE ELECTRIC FURNACE.

IN a recent publication of the United States Geological Survey, entitled "The Production of Phosphate Rock and Phosphorus in 1906," G. W. Stose gives an interesting summary of the progress made in phosphorus manufacture, and points out the rôle which the electric furnace has played in this development. Formerly phosphorus was only extracted from bones and other organic matter. It is only quite recently that it has been extracted from mineral products. First of all, phosphorus was extracted from phosphatic rocks, such as the impure fluophosphates of calcium, with which the superphosphates used in agriculture are generally made. Apatite, which is a fluophosphate or a chlorophosphate of calcium, was only used to a slight extent in Europe or in Canada. Quite recently wavellite (phosphate of alumina) has been used as a source of phosphorus. It is furnished in sufficient quantity for the purpose by deposits situated at Mount Holly Springs (Pennsylvania). The old process of phosphorus manufacture which was in use in the beginning of the nineteenth century is as follows: The bones are burnt, then ground; the bone ash or phosphate of lime is treated with a sufficient quantity of sulphuric acid to convert the whole or a part of the calcium into calcium sulphate and the phosphorus into metaphosphate of calcium or even into phosphoric acid, which is concentrated by evaporation, mixed with wood-charcoal and reduced by heating in a furnace in a fireclay retort. The vapour of phosphorus and carbonic oxide are given off. The phosphorus which is condensed under water has a waxy appearance and yellowish colour. Theoretically the reaction should be:—

$$2Ca_3(PO_4)_2 + 6H_2SO_4 + 10C = 6CaSO_4 + 10CO + P_4 + 6H_2O$$

Practically, however, it is found that the following reaction better represents what occurs:—

$$3Ca_3(PO_4)_2 + 6H_2SO_4 + 10C = 6CaSO_4 + Ca_3(PO_4)_2 + 10CO + P_4 + 6H_2O$$

In this process the loss due to destruction of the retorts by sulphuric acid and by the great heat is considerable. Only a portion of the phosphorus, therefore, present in the charge is recovered. There is also the danger of the phosphorus inflaming when withdrawn, and it is necessary to take the greatest care to prevent the phosphorus condensing in the tubes and obstructing them. Numerous improvements or alterations of this process have been patented in recent years. Woehler was one of the first to heat phosphate of lime as it occurs in bone ash or phosphatic rocks with silicious sand and charcoal without resorting to the sulphuric acid treatment. Wing's patent, 1891, is based on the same principle.

Wing's Process.—In Wing's process, bone ash or pulverized rock phosphate and silica are moistened and made into balls which are placed in layers alternating with layers of coal in a *cupola*. The coal yields the incandescent carbon required for the reduction of the phosphoric acid. The silica expels the phosphoric acid from the phosphate as anhydride, P_2O_5, which is reduced to the condition of phosphorus by the incandescent carbon and the reducing atmosphere. The vapours pass to condensation chambers kept at a temperature of 500° F. (260° C.), in which the greater part of the phosphorus is deposited as red phosphorus and the remainder in a water chamber as white phosphorus. The process is continuous, the charge being introduced at the top through the furnace mouth, the residues are evacuated by the grate at the bottom, and two condensation chambers are used alternately.

In using the ordinary furnaces this method was found impracticable owing to the high temperature necessary to treat a charge as refractory as that just indicated. It is well known that electricity can furnish the high temperature necessary, and it was well imagined that it ought to solve the problem, but manufacture by this process has only become possible commercially quite recently, since the invention of the electric furnace. Consequently, the process has been introduced both in Europe and America, where it enables phosphorus to be made at a profit.

Readman's Patent.—This process, which dates from 1889, is applied in most countries. The bone ash or the crude phosphoric acid is mixed with ground coal or wood-charcoal. If mineral phosphate be used it is roasted, pulverized, and mixed with wood-charcoal, silica, or a basic salt. The mixture is reduced in an electric furnace working continuously in a reducing atmosphere. The currents brought by retort carbon electrodes traverse the charge placed between them, which acts as a resistance and is heated to incandescence. The silica combines with the calcium to form a slag of silicate of lime. The phosphorus and carbonic oxide are given off as before described. The reaction commences at 1150° C., but a temperature of 1400° C., and even 1500° C., may be reached

before completion of the reactions. The reaction is the following:—

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C = 6CaSiO_3 + 10CO + P_4$$

Harding's Process.—In Harding's process of 1898, the pulverized rock phosphate is heated with sulphuric acid; the phosphoric acid thus separated from the lime is filtered and evaporated to a syrupy consistency. It is mixed with granular retort charcoal, heated in a reverberatory furnace, and treated in an electric furnace, the arc issuing impetuously between the electrodes and traversing the mass. An atmosphere of hydrogen is produced by injecting petroleum spirit in the form of a fine spray into the furnace.

Gibb's Furnace.—In this furnace, which was specially designed for the manufacture of phosphorus, the electric current, instead of traversing the whole of the mass, passes without interruption into an intermediate circuit of great resistance, such as a cylinder of retort charcoal placed above the charge. This cylinder becomes incandescent and the arch of the furnace deflects the heat as in a reverberatory furnace.

Irvine's Furnace.—Readman's process was modified in Irvine's 1901 patent. The charge is made up as in the original method; however, phosphates of alumina or calcium may be used indifferently with the silica or basic flux. The two electrodes of retort charcoal are suspended vertically, and their lower parts reunited at the beginning of the operation by coal through which the current first passes. When the charge has melted, the slag formed collects on the top and reunites the two electrodes; that is, henceforth it is through this slag that the current passes. The fusion is continued, the excess of slag is run off as it is produced, so that the extremities of the electrodes are never uncovered.

Duncan's Patent.—In Duncan's process, patented in 1903, seventy-seven parts of ground phosphate are taken, either of organic or mineral origin and twenty-three parts of ground coal, these being mixed with tar acting as an agglutinant. The paste is dried, and after heating, which is done for economy in a hydrogen flame, a by-product of the manufacture, the product is placed in an electrical furnace; this continuously produces phosphide of calcium. This phosphide, in contact with water in an atmosphere of hydrogen, gives off hydrogen phosphides which, when heated, are converted into red and white phosphorus according to the temperature at which condensation is effected.

Parker's Patent.—This process, which was patented in Great Britain by Parker in 1902, concerns the treatment of phosphate of aluminium. This phosphate is treated with sulphuric acid, then with a sulphate capable of forming an alum with the sulphate of aluminium, which is produced. All the alumina is separated by

crystallization of the alum, and before the electric treatment. The residual liquid is mixed with coal or other substances rich in carbon, and reduced in an electric furnace.

Landis' Method.—The American Phosphorus Company of Philadelphia possesses a factory at Yorkhaven where phosphorus is extracted from wavellite, using a method designed by G. C. Landis, the company's chemist. The process, which is kept secret, is, as far as can be ascertained, analogous to that of Readman as regards the mineral and the furnace. The wavellite (phosphate of aluminium) and the phosphate of calcium are roasted, mixed with silica and wood-charcoal, and reduced in an electric furnace which is one of the subjects of the invention. In January, 1907, a patent was taken out to protect certain improvements in the furnace, with the view of preventing the escape of gas or vapours or their absorption by the lining of the furnace. This is realized by the use of a second exterior lining made of non-absorbent bricks, and by the use of hydraulic joints for closing all the apertures of the furnace. The furnace is fitted with an interior lining of bricks of retort charcoal acting as electrode; there are also several vertical electrodes of the same material, which can be regulated either to establish a current through the charge or to form an electric arc. The slag is run off every three or four hours; the phosphorus vapours are condensed under water. It is very probable that it would be necessary to resort to a supplementary treatment to eliminate the alumina contained in the charge, and that the treatment is analogous to that used in the Parker process; this point, however, is kept secret.

The phosphorus made by the greater number of the industrial processes is a crude white phosphorus having the appearance of yellow wax, containing sand, charcoal, clay, and other impurities. These impurities are removed in different ways, either by filtering the fused phosphorus under water on wood-charcoal or through a cloth, or by pressing by means of steam the fused mass through porous porcelain, or by redistilling it in iron retorts. The best method of purification, however, is to treat the crude fused phosphorus, either by a mixture of bichromate of potash and sulphuric acid, or by hypobromite of sodium. Some of the impurities dissolve, the others collect as a scum which floats to the surface of the fused phosphorus. Owing to its highly poisonous nature, and the danger in manipulating white phosphorus, attempts have been made to produce it in another form. Red phosphorus, which is not poisonous, is easily prepared by heating to 250° C. the white variety in an inert gas in a closed vessel. It, however, has not the same properties as the crystalline white phosphorus. A crystalline variety of red phosphorus, recently discovered in Germany, is obtained by heating to boiling a 10 per cent solution of white phosphorus in phosphorous tribromide. This variety is

not poisonous, and advantageously replaces white phosphorus in the manufacture of matches. The phosphorus industry is so recent in France that it is very difficult to get statistical figures; moreover, information is meagre on the state of the industry in other countries. The world's yearly production has been estimated at between 1000 and 3000 tons; up to quite a recent period this manufacture was localized abroad. The greater part of the world's phosphorus comes from the factory of Allbright & Wilson of Wednesfield, Oldbury, England; it was there that the Readman process was developed. Its annual production may be 500 tons. There are other big factories at Lyons, France, at Griesheim and at Frankfort, Germany. There is likewise a factory in Sweden, and others, small and numerous, in Russia, of which six, situated near Perm, produced about 140 tons in 1890. In the United States, the first phosphorus factory was constructed forty years ago at Philadelphia, by Moro Phillips; this establishment is still at work. The factory of J. J. Allen & Son was founded at Philadelphia in 1891, and in competition with imported phosphorus has furnished for a long time the phosphorus required by the Diamond Match Co., the largest match factory in the United States; but in 1897, the firm of Allbright & Wilson, under the trade name Oldbury Electro-Chemical Co., erected a factory of 300 H.P. working the Readman process at Niagara Falls, and it is this factory which up to now has supplied the Diamond Match Co., and furnished the greater part of the phosphorus produced in the United States. Recently that company has brought a new improvement to bear on the manufacture, installing Irvine's furnace, by means of which 80 to 90 per cent of the phosphorus contained in the raw material used can be extracted, which is a high strength rock phosphate. This result is comparable to that which the English factories obtain, extracting 86 per cent of phosphorus. There are six furnaces of 50 H.P., each with a production of 170 lb. of phosphorus per day, say an average total of 1000 lb. of phosphorus manufactured daily. The production varies according to the demand; however, the factory turns out at the present time half of that which is produced in the United States.

The General Chemical Co. has recently acquired Duncan's patent, and another company is installed at Long Island, where they utilize for their furnaces the current which is distributed in the town.

The American Phosphorus Co. made its first installation at Moore's Mill, near to Mount Holly Springs, Pennsylvania, where there is a mine of wavellite, which it possesses. The old method of heating by gas is used. The factory having been destroyed by a fire, another was constructed and started in March, 1905. Electric furnaces were installed and working during 1905, but the production

of electricity by means of steam engines was found too costly, and in 1906 the factory was transferred to Yorkhaven, Pennsylvania, where electricity yielded by water-power could be used. This company announces that it produces 500 lb. of phosphorus a day, and that it could produce 1200. The census of 1900 states that three factories were at work in the United States, but that of 1904-1905 shows only the Oldbury Electro-Chemical Co. of Niagara Falls. Besides the home production the United States annually imports 30,000 to 40,000 lb. of phosphorus, which pays an import duty of 18 cents per lb.

CHAPTER X.

MANUFACTURE OF BONE DUST AND OF BONE SUPERPHOSPHATE (VITRIOLIZED BONES).

THE use of bone dust as a manure goes back to somewhat distant times. It rapidly extended when Liebig advised that it should be dissolved by sulphuric acid, so as to obtain more rapid and certain effects. At the present time this product has to compete against nitrate of soda and basic slag. Moreover, certain manufacturers find it more advantageous to use bones in the manufacture of glue, and to transform them into superphosphate afterwards. Whatever be the method of utilizing bones, it is indispensable previously to free them from fat, as will be seen in the sequel.

Chemical Composition of Bones.—The bones which form the framework of vertebræ, consist like all vegetable and animal matter of organic elements, and of mineral elements or of combustible matter, and of ash. The combustible matter consists essentially of ossein (yielding gelatine) and of fat. Bone ash is composed in great part of phosphate of lime. If the previously fat-extracted bones be digested with dilute hydrochloric acid, the phosphate of lime is dissolved, and a residue of ossein is obtained as a white elastic translucent substance which consists of:—

TABLE XLVIII.—CHEMICAL COMPOSITION OF OSSEIN.

	Per cent.
Carbon	50·1
Hydrogen	7·1
Nitrogen	18·8
Sulphur	0·2
Oxygen	24·2
	100·4

Ossein dissolves very slowly in boiling water when bones are boiled with water, and more rapidly when treated in a closed vessel under pressure. By prolonging the operation for a sufficient length of time the bones can be completely freed from ossein. A residue of phosphate of lime is thus obtained still retaining the original form of the bone. Finally, ossein may be extracted by boiling with

dilute potash lye. On cooling, the solution of ossein previously concentrated by evaporation assumes a gelatinous consistency, and on drying it is converted into solid tablets which are marketed as glue. The ratio between the organic substance and the mineral matter in bones continually varies, not only with the origin and race of the animal from which they come, but also in one and the same individual, according to whether the bones are hard or spongy. In spongy bones the organic matter is higher by 4·5 per cent than in hard bones; the amount of carbonate of lime is likewise higher by 11 per cent, whilst the percentage of phosphate of lime is less by 15·5 per cent. It is evident that the percentage of nitrogen and phosphoric acid in bones is very variable. Their fat content, calculated on the dry substance, is from 10 to 12 per cent. Berzelius has given the following analysis of an ox bone freed from periosteum :—

TABLE XLIX.—ANALYSIS OF AN OX BONE. (BERZELIUS.)

	Per cent.
Cartilage completely soluble in water, Vessels " " " "	33·30
Tribasic phosphate of lime and a little CaF_2	58·35
Carbonate of lime	3·85
Phosphate of magnesia	2·05
Soda with very slight trace of NaCl	2·45
	100·00

This analysis of bone being that of a select bone does not represent the average composition of the bones used by glue manufacturers, because the bones have undergone various treatments, such as boiling or fermentation, which may have altered their nature. Besides, bones are derived from different animals. Practically ordinary bones received in factories respond in round figures to the following analysis :—

TABLE XLIX. (A).—AVERAGE ANALYSIS OF BONES AS SUPPLIED TO MANURE FACTORIES.

	Per cent.
Moisture	12
Organic matter	28
Tribasic phosphate of lime and magnesia	44
Fat	10
Carbonate of lime, sand, etc.	5
	99

Commercial bones always contain more or less moisture, butchers' bones up to as much as 30 per cent, and they are mixed with other waste such as debris of skins, gut, etc. It is not easy

to get an idea of the quality by analysis owing to the difficulty of taking a fair average sample. The skill and experience of the buyer after inspection are the best guides.[1] Fossil bones naturally differ from fresh bones in their composition, thus their fluorine content rises to as much as 16 per cent. Müller found 17 per cent of gelatine in diluvian bones.

Fertilizing Value of Bones.—The use of bones as a manure has been known for a long time. They have been used for centuries in the manuring of vines in the south of France. Hunter, in England, drew the attention of farmers to the value of bones in 1774. In that country the use of bones doubled and trebled the production of mediocre land, at a time when certain continental agronomists were still protesting against what they called the spoliation (*gaspillage*) by the bones used in fertilizing the land. England profited by this situation, importing thousands of tons of bones at a very low price. At a certain period all the production of bones took the road to Great Britain, although it had itself an enormous production, and in spite of a rise in freights. In 1822, the battlefields of Central Europe, in themselves alone, furnished her with 33,000 tons.

But the introduction of Peruvian guano, the pioneer of all other concentrated manures, completely altered the situation. There is not now to be found a single farmer who gives to bone manures all the credit which they deserve, even when he is not indifferent to other manures. However, uncrushed raw bones are relatively valueless to the farmer, since they do not become soluble in the soil until after a very long time. Now, in order to obtain good crops, the farmer requires rapid decomposition of the nitrogenous matter and absorption of the phosphate in the soil. The bones must therefore undergo an appropriate treatment. In chemical manure factories it is reduced to a fine powder or the gelatine is extracted from it, and it is afterwards made into superphosphate (dissolved bones). The use of bones in any other form is to be deprecated. Bone waste (fleshy fibre), which can be often bought cheap, should be similarly treated.

Storing, Classifying, Sorting, and Crushing Bones.—Storing.—The first duty of the manufacturer is to bring all his experience to bear on the storing of bones, because when they begin to rot they give off a smell which is very obnoxious to the workmen. Besides, the decomposition of the nitrogenous matter gives rise to a disengagement of ammonia, and there is thus a loss of nitrogen which may exceed 0·5 per cent. The drying of fresh bones requires careful and costly manipulations; that is why they rest content with sprink-

[1] For further analyses of bones, see "Bone Products and Manures," by Thomas Lambert, published by Scott, Greenwood & Son, London.

ling them with water containing 0·05 per cent of carbolic acid or with spirits of turpentine.

Classification of Bones.—Market bones are classified as follows:—

(1) *Kitchen Bones.*—These consist of ox, calf, sheep, goat, and some game bones. They may be fresh, dry, or fermented. They often contain 20 to 25 per cent of water. Dry bones are called country bones. Their content of moisture is from 8 to 12 per cent. They are generally crushed and often fat-extracted by the vendors, which is readily recognized by the opaque whiteness of the bones on the outside. Fermented bones enter into the class of the fossil bones; they are unfit for glue-making, for the organic matter has in great part disappeared owing to decomposition and exposure to all sorts of weather. Amongst kitchen bones are to be found sheep bones and those of kids, and pork bones, which are less esteemed. Kitchen bones generally contain remains of horns, hornpiths, hair, glass, scrap iron, earth, bread, etc. Hand picking considerably enhances the value of the goods.

(2) *Horse Bones or Knackers' Bones.*—These bones yield a less valuable glue than kitchen bones, and they have to be sold cheaper. Ten per cent of these bones are tolerated amongst kitchen bones. The fat and glue which they yield are inferior.

(3) *Buried Bones.*—Buried bones are those of animals (ox, horse), which have remained a certain time in the ground to destroy the flesh. They are the bones of infected animals which have assumed a bistre colour owing to contact with the humus in the soil. They are depreciated and the manufacturer refuses those with adherent flesh.[1]

(4) *Bullocks' Heads and Canards (Sheep's Heads)* pass into the kitchen bone class, but they are generally sold apart for the acidulator.

(5) *Scraps and Waste.*—These are the residues of the "turnery" trade. They are in great request for acidulation and are sold separately.

(6) *Hornpiths.*—They are used like "scraps" for acidulation. They are fresh or dry. The dry piths are often fermented and are then of less value.

Bones, therefore, in consequence of the different material which they contain, are classed and assorted so that the operations which they have to undergo may furnish satisfactory products. As the bones are most often mixed with impurities which are of a nature to damage the machines, it is necessary to pick or assort them.

Bone Picking.—In some factories the picking is done on shaking

[1] The resurrection of the bones of infected animals is a most dangerous practice. The earth mould from the remains of animals which have died of anthrax is still infectious after twenty years.—TR.

tables, driven mechanically or by means of large sifting machines, both appliances being fitted with wire netting having meshes of $\frac{2}{5}$ of an inch. Soil and small particles of bone fall through the grating, whilst horns, glass, and scrap iron are separated by hand on the shaking table, or on a revolving table placed at the end of the shaking table, or the sifting machine. Generally, they rest content with receiving the bones on an inclined endless band, along which the female sorters are arranged. The band moves slowly, so as to give time for sorting, and its slope enables the bones to feed into the hopper of a bone crusher. Before falling into the crusher, the bones issuing from the band fall on to a narrow iron plane inclined at 45°, divided into two parts soldered by a copper band. Each of these parts corresponds to one of the poles of a strong electro-magnet situated underneath. It follows that if the iron falls on the inclined plane it is retained, and eliminated by the sorter who had allowed it to pass from the band. In this method of sorting, the earth necessarily follows the bones into the crusher; nevertheless, a certain part of the earth is removed before passing on to the band when the man feeding uses a fork with close teeth in shovelling the bones which have been thrown on to a perforated sheet of iron over a pit where the earth collects. Although this earth may be removed in subsequent operations, it is always more advantageous to remove it before crushing, so as not to have pulverulent matter in the fat extraction and in the glue autoclaves. There is little useful matter in this earth, from which the small particles of bones are subsequently removed by finer sifting. They are mixed with bone meal for manure.

Bone Crushing.—Two kinds of machines are used in bone crushing; one working at a slow speed, which is the toothed crusher, and the centrifugal crusher at great speed, as, for instance, that constructed by Weidknecht. It is well to have several successive crushers with duplicate spare parts, so that if they should get damaged they may be replaced rapidly. The first crusher is the coarse crusher, and the second the finishing mill.

(1) *Slow-speed Crusher.*—This consists of two large rolls formed by thick circular toothed discs with teeth a little obtuse, alternately with plain discs of the same thickness, but of a less diameter by the height of two teeth; the discs are mounted on a hexagonal steel axis to form a roll. The rolls are fitted up in such a manner that the teeth of the one correspond to the circular part of the smaller diameter of the other. They are separated by the space required, to crush either coarser or finer. For that purpose, they are driven by steel cog-wheels with deep teeth, which allow a certain displacement. One of the rolls is on movable bearings, capable of sliding if the resistance to be overcome is too great, being brought back to the original position by a system of springs.

A good flywheel is necessary to overcome passing obstructions. The crushers built by Krupp attain the same end, and are made of very hard special steel. There are two crushers, one following the other, fed by cup chain elevators in the case of the second crusher, so as to arrange two pairs of rolls on the same framework. The second crusher has shorter teeth, and its rolls are nearer. The largest pieces issuing from the second roll must not be larger than a small hen's egg, in order to ensure subsequently a perfect fat extraction.

(2) *Very Quick-speed Machine.*—To this class belong Weidknecht's (F.) and Carr's. Weidknecht's excellent crusher consists of a very strong framework, properly so-called, of cast-iron in two pieces, the lower part or pedestal, and the upper part or hood; these pieces are bolted at their point of contact. The hood is adjusted to the framework, on the one hand, by a joint forming a hinge, and on the other hand by a screw and bolt joint. By this arrangement a single workman is able to inspect the machine, or change the grating in a few minutes. All that is required is, by a turn of the spanner, to reverse the screw of the bolt joint, and to lift the hood which hinges on its axis. The bearings are large and require constant lubrication. Moreover, to diminish the friction surface of the shaft, the plummer blocks are suppressed, and to keep up the lateral play they are replaced by abutment screws which are fitted to each end of the shaft and in contact with the tempered sheaths adjusted consequently in the end of the shaft.

The shaft thus maintained is filled in its middle with a jacket or boss, on which fixed levers are arranged, at the end of which levers hinged hammers are fixed which work like flails, the hinge enabling the hammer to fold itself back when at work if there is too much feed or if a foreign body should get into the machine. The mobility is also intended to keep the machine from stopping if the belt comes off, if it be not fed regularly. In fact, the hammers, by folding backwards, allow the fine material to pass through the grating arranged in the lower part of the framework; the apparatus being thus freed, the shaft regains its normal speed without having to stop. The hammers thus form a fly-wheel, storing up active energy. The machine is fitted on its interior lateral faces by toothed steel plates of great hardness; these are held in position by bolts and can thus be easily replaced. The hood or upper part is fitted up in the same way on its lateral faces; moreover, it has on the roof linings, likewise fitted with projections, and fixed by bolts on the shaft is the driving pulley. The machine is in fact very strong, and the pieces easy to replace. There is no heating in spite of the speed, for the ventilation due to the motion is very energetic. The fineness of the product depends solely on the dimensions of the grating, which in the case of bones consists of bars wide apart,

through which the hammers drive the crushed bones. A crusher with bars set closer acts as a final crusher, and, as before, a chain cup elevator serves to feed the second with the crushed bones from the first after they have been through a sifting reel.

It is asserted that crushers working by shock develop more heat than need be. With crushers such as those described working at a great speed, with the bars of the grating far apart, the temperature does not rise more than with a toothed cylinder, for the ventilation is very energetic and the friction reduced by the width of the passages.

Extraction of Fat from Bones.—The extraction of fat from bones is an indispensable operation, even when it is a question of merely converting the bones into dust for the farmer. In fact, bone dust not deprived of its fat is of less value, because the fat decomposes very slowly in the soil, and constitutes an obstacle to the phosphoric acid becoming soluble.

Fat may be extracted from bones by three processes: (1) By simple boiling in open pans. (2) By the action of steam in closed vessels. (3) By solvents. The extraction of fat by simply boiling leaves the ossein almost intact, but generally there is only obtained a portion of the fat from the bones.

By extracting the fat by steam, a higher yield of fat is obtained, especially if the operation be continued for a sufficient length of time, but a portion of the ossein is then transformed into gelatine. Now, in manure manufactories this gelatine constitutes a loss and becomes cumbersome because it decomposes rapidly; if it be diverted into a stream, it infects the rivulets. It is best used in irrigation. Bone dust from bones treated by steam is more soluble than that of bones from which the fat has been extracted by simple boiling; moreover, it is also more in request by farmers.

But this preference is not justified, for bone dust from steam-extracted bones is less rich in nitrogen. The extraction of bones by solvents (benzene, petroleum, ether) gives a larger yield of fat whilst preserving integrally the ossein of the bones; these then form a powder rich in nitrogen. This process is undoubtedly to be preferred whatever may be the further treatment (manufacture of gelatine, or manufacture of manure). It is the only rational process to apply.

Extraction of Fat from Bones by Water.—This process is the most ancient, and recalls to mind the skimming of the cook's "stock" pot. In a cylindrical cast-iron pan a little wider below than above, there is introduced by means of a crane a basket of perforated wrought-iron containing about one-half ton of bones. The bottom of this basket, likewise perforated, opens in the form of two semi-circular parts held by hinges on a cross-bar, dividing the basket into two equal parts. These two doors are closed by hooks,

so as to bear the weight of charge. The basket is cylindrical, a little smaller in diameter than the pan which contains it, and shorter by 4 inches. A strong circular hoop at the top supports the sheet iron, and carries four strong handles, by means of which the cross-piece of the crane can lift it. The cast-iron pan is fitted with a gutter or throat, so as to separate the fat from the water in a continuous manner. The basket, therefore, being charged with bones in the fat extraction pan, water is run in to immerse the bones and steam caused to bubble in the bottom from a perforated steam coil. The water, brought to about 100° C. (212° F.), causes the fat to rise from the bones through holes in the gutter at the same time as the excess of water. The fat flows constantly from the gutter by the horizontal exit tube, whilst the water in the bottom issues through a bent tube without taking any fat with it. The exit of the fat may be facilitated by a superficial push, or by a paddle driven mechanically, mounted on a vertical shaft fixed on the side of the pan, capable of being rotated and which may be raised at the end of the operation, so as to allow the basket to be freely removed from the pan. The bones are extracted in this way for about an hour and a half, after which they are removed from the basket to the washer. In some factories the water is slightly acidulated by an addition of sulphuric acid, 4 litres for 500 kg. of bones (about 1 gallon for ½ ton), so as to free the grease from its calcareous compounds. There is obtained 1 to 5 per cent of fat according to the quality of the bones. The same water may be made to serve for several successive operations, and finally forms a batch of gelatine size sufficiently concentrated for making glue. If gelatine is not manufactured the boilings are collected and concentrated by evaporation and added to the bone dust as shown in the sequel. But the same water cannot serve indefinitely for fat extraction. After a certain time, it is remarked that the fat which it removes no longer rises to the surface. The solution assumes a milky appearance, which is a sign that it is saturated with gelatine and that its concentration obstructs the ascent of the globules of fat. It must then be drawn off and replaced by fresh water. Unless fresh bones are operated on, the fat obtained on extraction by water is generally of inferior quality; it has a bad odour and is more or less dark in colour. It is purified as indicated later.

Fat Extraction from Bones by Steam.—Fat extraction from bones by steam is performed in large cast-iron cylinders, capable of containing 4 to 5 tons of crushed bones, the upper opening serving for the introduction of the bones, the lower opening for their discharge. These openings are closed by hinged lids as in an autoclave. Steam enters at the top and the fat runs off from the bottom by means of pipes situated near the aperture. Steam of from two to

four atmospheres is used; for one to two hours the steam carries the fat with it. The condensed water, charged with fat and gelatine, collects in the space reserved below the false bottom and is afterwards added in the manufacture of nitrogenized superphosphates, although the fat exercises an unfavourable influence on the dissolving of the phosphate. This water generally contains 1 to 2 per cent of nitrogen and 0·3 per cent of P_2O_5. In the concentrated state it contains as much as 7 per cent of nitrogen, 3 per cent of ash, 50 per cent of organic matter, and 45 per cent of water. The solution of fat and gelatine is withdrawn from time to time, and the treatment by steam continued until a sample of the liquid contains no more fat. To separate the two, the different draw-offs are united in a wrought-iron pan with a conical bottom, fitted with a steam jacket into which steam is injected, and a tap near the top for drawing off the fat. The object of heating is to keep the gelatine fluid enough to allow the fat to separate on standing. When separation is complete, the fat runs off by the above-mentioned tap, and the gelatine is run into an evaporation pan through a valve in the conical bottom of the pan. Whatever may be the quality of this gelatine, it may be of advantage to reduce it to a marketable form by a series of manipulations which the author has described elsewhere. By submitting bones to systematic treatment, all the gelatine may be extracted, and the resulting bone dust, almost destitute of nitrogen, contains 35 per cent of phosphoric acid. Bone dust is often mixed with moist superphosphate to dry it.

Some manufacturers make only degelatinized bone dust which constitutes an excellent food for animals and a very active chemical manure for meadows.

The fat extracted from bones by steam has approximately the same colour as that obtained by boiling, but it is of better quality and has a less unpleasant smell. When the bones operated upon have commenced to decompose, as very frequently is the case, the evil-smelling products are in great part volatilized during the operation. Bang and Ruffin have suggested steaming combined with centrifuging. The fat with a little gelatine can first be extracted in a centrifugal machine, then the gelatine. This process has not been adopted by bone-boilers, but it is used in extracting fat from fish waste.

Extraction of Fat from Bones by Benzine.—For a long time efforts were made in France to extract fat from bones by benzine. Deiss used carbon disulphide, but as the bones, after extraction with this solvent, yielded low quality glues, the process was abandoned. In 1871, Vohl suggested canadol (gasolene) as an advantageous substitute for carbon disulphide; then in 1876 M. Terne took out a patent for extraction by petroleum benzine, in America, whence this industry spread to Europe. Petroleum benzine is somewhat

less dangerous than carbon disulphide, and its condensation is easier because it boils at a higher temperature. The apparatus constructed by Mr. Deroy, sen., for extracting fat from bones by petroleum benzine consists essentially (Fig. 36) (1) of an extractor A with a perforated false bottom, and steam coil; (2) of a re-

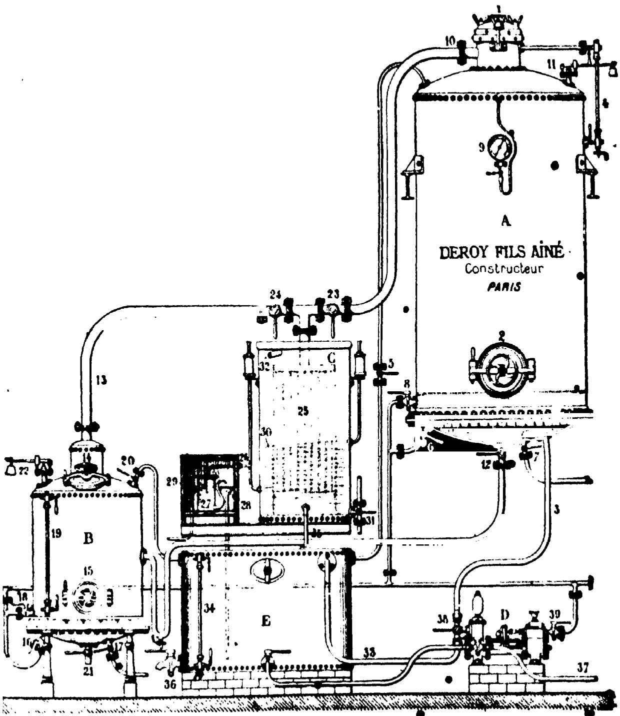


FIG. 36.—Plant for Extraction of Fat from Bones by Petroleum Benzine.

cuperator B or distilling pan; (3) of a condenser C; (4) of a pump D for circulating the solvent. *Working.*—The routine of the operation may be outlined thus. A certain amount of water is run into the extractor according to the capacity of the apparatus, so as to preserve the coil and the taps from the attack of fatty acids. Afterwards, the extractor is charged with crushed bones free from foreign

matter. As soon as the charge amounts to a quarter of the capacity of the apparatus, the pump is started, and a beginning made by drenching with benzine the bones introduced. During this time the autoclave is charged in such a way that the solvent constantly bathes the bones, which enables the interposed air to escape freely. When the apparatus is full the cover of the extractor is closed and the tap 23 on the condenser opened. The air is allowed to escape until condensed benzine appears; the tap is then turned and the pressure allowed to rise to $1\frac{1}{2}$ kgs. on the manometre (9). This pressure once reached, the steam tap is closed and the apparatus allowed to rest till morning. The benzine is charged with all the fat of the bones, and the vapours are totally condensed. The next morning the apparatus is emptied into the distilling pan, and after a rest—about ten minutes—the water, previously run into the autoclave, and which now occupies the bottom of the pan, is withdrawn. The benzine is then recovered by distillation and by passing it through the condenser C, by means of the gooseneck 13, and the tap 24; it goes to the reservoir E. The benzine impregnating the bones is subjected to a current of steam, which finishes by carrying it into the distilling apparatus. When it has been made certain that nothing but water passes in the distillate, the extractor is emptied, first opening the lid of the upper manhole, and then the bottom one. The distillation is urged until no more petroleum benzine distils. At this moment a current of steam is injected into the fat by means of a perforated steam coil which carries off the last traces of solvent. The fat can then be drawn off from the distilling pan by the tap 21.

Purification of Bone Fat.—Fresh bone fat is naturally whiter than the fat from ordinary country bones. It is purified by treatment in a lead-lined pan, with water acidulated with sulphuric acid, of which an excess must not be used. The fat and the acidulated water are then heated by a perforated steam coil, which agitates the two together. After some time the tallow shows clear and no turbidity appears in the spoon. The steam is then shut off and the whole allowed to stand. The mixture of tallow, gelatine, organic matter, and phosphate of lime, and of fatty acids combined with lime, is destroyed, the gelatine is attacked by the acid, and the lime is precipitated as sulphate of lime with various impurities. After sufficient resting, the layer of fat is separated by means of a pipe hinged to the draw-off tap which is at such a level that it enables the pure fatty layer to be run off the surface, water and sulphate of lime remaining behind. The purified grease falls into a wooden vat lined with lead, where it is washed several times with boiling or simply tepid water. After which it is allowed to stand and drawn off as before into casks for use in soap works or candle works.

Bone fat is often bleached as follows:—

To the melted fat mixed with half its volume of water, 2·5 per cent of chlorate of potash is added and enough hydrochloric acid to decompose the whole of the chlorate. An excess of this acid is added to neutralize calcareous compounds. The fat is purified and whitened with 2·5 per cent of chlorate and a semi-tint obtained; with 5 per cent of chlorate a whiteness of the fat is obtained analogous to that of lard. It is washed several times with water, until the wash water is free from chloride, which is recognized by iodide and starch paper. Bleaching by sunlight is equally energetic. The fat must be run into shallow vats which are exposed to the light. Agitation in presence of ozonized air also constitutes a method of bleaching. At the normal temperature bone fat is soft, unctuous, and does not easily become rancid. Although insoluble in water, it contains about 2 per cent of water, which it is impossible to eliminate even by heating to 100° C. To obtain it in an anhydrous state, it is necessary after having refined it to heat it up to 150° C., and to maintain it for some time at that temperature. But it is easily disposed of even when it contains a little water.

Manufacture of Bone Dust.—Fat-extracted non-degelatinized bones are reduced to powder which passes through a No. 50 sieve and dispatched to farmers without other treatment. If, on the contrary, the bones have been deprived of the greater part of their nitrogen, they decompose with difficulty in the soil, and it is then better to convert them into superphosphates. The crushers used being the same in both cases, the reader is referred to the description already given. The mode of action in the soil of the non-degelatinized bone dust is based, in the first instance, in the solubility of phosphate of lime in putrefying gelatine. It behaves to a certain extent like raw Peruvian guano, which has already been described, and in which the basic phosphate of lime is rendered soluble by the nitrogenous elements which accompany it. The bone dust in the soil, owing to its relative insolubility, is distinguished by this peculiarity, that its phosphoric acid is not readily extracted by the soil; it can thus penetrate into the deeper layers, whilst every other form of phosphoric acid is utilized in the surface soil. This property of bone dust is sometimes of great benefit to the farmer. The cropping in the same soil during several successive years of plants with tap roots may have exhausted the subsoil of phosphoric acid. In that case bone dust furnishes the means of replenishing it with that element so necessary to vegetation. The finer the bone dust the more easily is it dissolved and decomposed. Coarse powder only acts feebly, but its action is appreciable for several years. The fine powder decomposes rapidly in the soil and acts energetically the first year. That is why farmers always require a fine powder. It is to the interest of the manufacturer to suit them by attending to

the crushing and the grinding of the powder. Bone dust made from fat-extracted bones has the following composition, according to Holdefleiss :—

TABLE L.—ANALYSIS OF BONE DUST FROM FAT-EXTRACTED BONES.

	Per cent.	
Nitrogen	4·14	
Phosphoric acid	21·68	45 per cent $Ca_3P_2O_8$
Water	6·51	and 1·49 per cent $Mg_3P_2O_8$
Organic matter	36·29	
Carbonic acid	2·30	
Sulphuric acid	0·41	
Lime	27·83	
Magnesia	0·68	
Oxide of iron	0·37	
Fluorine	0·52	
Sand	3·60	

Stored and fat-extracted bone dust does not contain more than 2 to 3 per cent of fat.

The efficiency of bone dust as manure has been the subject of many discussions. P. Wagner and Mercker seem to have under-estimated its fertilizing value, whilst other experimentalists have obtained excellent results. According to recent experiments, it is recognised that the efficacy of bone dust was perceptibly increased by an addition of solvents; nitrifying bacteria likewise intervene. A small quantity of the solvent (sulphuric acid) suffices to give to bone dust a remarkable activity, as experiments on this point testify. This agent has the effect of disintegrating the bone dust, and rendering it soluble in citrate. Stoved bones, neither fat-extracted nor degelatinized, do not dissolve in a satisfactory manner. The organic matter of such bone dust is transformed into a gluey matter very difficult to dry.

Classification of Bone Dust.—J. Konig has proposed the following classification of bone dusts :—

1. *Normal Bone Dusts, or Bone Dust No.* 0.—Those bone dusts which are made from bones which have not undergone any treatment for the extraction of gelatine, containing 4 to 5·3 per cent of nitrogen and 19 to 22 per cent of phosphoric acid, in which, moreover, after deduction of the matter extractable by chloroform the two factors are as 1 : 4 to 5·5.

2. *Bone Dusts (without any other designation).*—Those bone dusts which contain 3 to 4 per cent nitrogen and 21 to 25 per cent of phosphoric acid, and in which after deduction of the matter extractable by chloroform, the ratio of the nitrogen to the phosphoric acid is 1 : 5·5 to 8·5.

3. *Degelatinized Bone Dusts.*—Those which contain 1 to 3 per cent of nitrogen and 24 to 30 per cent of phosphoric acid, and in

which after deduction of the matter extractable by chloroform, the ratio of the nitrogen to the phosphoric acid is 1 : 8·5 to 30.

To these kinds of bone dusts must be added the bone dust made in some countries from raw bones. However, there is sometimes sold as raw bone dust the waste from bone-black making, after the extraction of the fat by benzine. Nothing should be designated as raw bone dust unless actually made from raw bones. [The bone-black factories sieve the bone dust from the meal or granules before charring the bones, as the dust is not so efficacious a decolorizer as the granules.]

4. *Mixed Manure Dusts.*—The manure dusts which after deduction of the matter extractable by chloroform containing 1 per cent of nitrogen as ossein, and in which the ratio of nitrogen to phosphoric acid is from 1 : 30, should not be designated as *bone dusts*, but as *mixed manure dusts.*

Meat Dust (*Meat Meal*).—An exception to this rule is formed by the manure prepared in the manufacture of meat extract, and which ought to be designated as meat dust (meat meal), which sufficiently differentiates it from the above-named bone dusts. Thus established, the differentiation of the different qualities of bone dusts is very sharp, and they are no longer confused with mixture of horn, hair, etc.[1]

Adulteration.—Bone dust is the subject of numerous sophistications. Finely crushed gypsum and corozo (vegetable ivory) powder are often found therein, substances which it is impossible to recognize by the naked eye. In that case the analysis of the product shows that its percentage of nitrogen and phosphoric acid is inferior to the normal, for corozo only contains 2·44 per cent phosphoric acid and 0·96 per cent nitrogen, and gypsum contains neither of of these ingredients. But the most frequent adulteration consists in adding to it phosphorite, or the phosphatic lime of the glue manufacturers, or a mixture of phosphate of lime and greaves. As all these products are rich in phosphoric acid, their effect is to increase the total phosphoric acid of the product, and to diminish considerably its percentage of nitrogen. To hide as much as possible the difference between the two elements which would be revealed by analysis, sophisticators resort to sulphate of ammonia. But, as already pointed out, the essential element besides phosphoric acid is ossein, or gelatine, which cannot be replaced by nitrogenous debris of animal origin, and far less by sulphate of ammonia. The above sophistications are therefore very prejudicial to the farmer, even if he receives in that way more nitrogen and phosphoric acid than furnished to him by normal bone dust. The mixture of phosphorite or of phosphate of lime and ammoniacal salt can never

[1] For analyses of boiled and steamed bones, benzine extracted bones, see "Bone Products and Manures," by Thomas Lambert, published by Scott, Greenwood & Son, London.

replace bone dust. No more can the mixture of phosphate of lime and greaves replace it, for the nitrogenous elements of this mixture do not consist of ossein, but rather of a substance analogous to horn.

As regards the impurities, sand, etc., and the degree of moisture they should not exceed certain limits. Like all pulverulent substances, bone dust absorbs moisture from the air and the manufacturer cannot be responsible for it. The normal moisture is 4·7 and the percentage of sand 2·4 per cent.

Manufacturing of Bone Superphosphates.—As just observed, bone dust differs in composition with the nature and quality of the bones from which it is derived and the method of manufacture. In normal bone dust, the ratio of the nitrogen to the phosphoric acid is as 1 : 5. Generally, however, there is found 0·5 to 1·0 per cent of nitrogen from different debris of animal origin. Bone dust of this nature may be delivered to farmers without other treatment. But if the ratio between the nitrogen and the phosphoric acid is less, say 1 to 6, or beyond (Holdefleiss found a sample was 1 : 23·55), it is a proof that the bones were too much degelatinized, and the dust is of less value if used directly as manure. It would behave in the soil like a mixture of normal bone dust and phosphorite powder, or if its percentage of nitrogen has been artificially increased, as a mixture of normal bone dust, phosphorite and of dried blood. All the phosphoric acid in excess above the ratio of the proportion of ossein nitrogen to phosphoric acid should be regarded as raw phoshate, and of no value to the farmer.

But these kinds of bone dusts yield excellent results if converted into superphosphates. In fact, if all the phosphoric acid be dissolved, the latter has no need of ossein in the soil; the bone dust so treated constitutes a nitrogenized superphosphate. The manufacture of bone superphosphate (pure dissolved bones) is very simple at first sight. The bones, previously crushed and degreased, are reduced to powder by means of a steel ball mill, or by a Carr's disintegrator. The powder yielded by the crusher is then passed through a No. 50 sieve, and the core returned to the crusher, which finally reduces it to the desired fineness.

The bone dust is then mixed with the desired amount of dilute sulphuric acid, using the same mixer as in making mineral superphosphates. But bone dust does not behave nearly so well as mineral phosphate under the action of the sulphuric acid. It has already been pointed out that mineral superphosphates contain free phosphoric acid, which renders them moist to the touch. To this drawback, another is added in the case of bone superphosphate, the sulphuric acid converts the organic matter into a viscous mass, which prevents the drying of the superphosphate. Also, owing to the fact that the action of the acid is very energetic and the mass

swells considerably it is necessary to place a much smaller charge in the mixer. It may also be remarked that the mixture tends to set rapidly, and this may need the addition of more water than is altogether desirable in order to keep it sufficiently fluid to run out.

A multitude of methods have been tried to eliminate this drawback, but the greater number have failed. In this way it has been tried to dry the superphosphate with sand, lignite, ash, and other analogous pulverulent matters. But the addition of all these substances not only diminishes the percentage of nitrogen, but it opens the door to sophistication of all sorts. It has been given up.

Another way of attaining the same object, proposed by Rumpler, was the use of bone-black. As this material possesses considerable absorptive power for liquids, it may be successfully used to dry manures with a tendency to remain damp. The bone-black is incorporated thus: The bone-black is first incorporated with the quantity of sulphuric acid required to dissolve its phosphate, at the same time as that for the bone dust. When the decomposition of the black is finished, the bone dust is incorporated with the mixture. If any insoluble phosphate remains undissolved, it is bone phosphate, which becomes readily soluble in the soil. Bone-black, however, has the decided disadvantage that it produces a black manure to which the farmer strongly objects, believing that it contains soot; the best material to use for drying the manure is bone ash, which is almost white.

If it be desired to increase the amount of nitrogen, the gelatine extract obtained by steaming bones may be added to it. But, so as not to introduce too much water into the manure, care is taken to reduce its volume to a third by evaporation, and to use sulphuric acid of high strength. Finally, it is preferable to secure the drying of the phosphate by only dissolving it incompletely. In that case, only $\frac{2}{3}$ or $\frac{3}{4}$ of the sulphuric acid required for completely dissolving the phosphate is used.

Again, the addition of a little nitrate of soda 1 : 2 per cent considerably accelerates drying, but the evolution of nitrous fumes must then be taken into accouht, as they are very injurious to the work-people and moreover constitute a loss.

Bone superphosphate dries spontaneously in the heap, and at the end of a month the reactions of which it is the seat are terminated. It suffices then to pass it through a Carr's crusher, and to sift it to reduce it to a pulverulent form.

Mixture of Bone Superphosphate (Dissolved Bones) and Nitrogenous Matter.—Bone dust from steamed bones contains on an average only 3 to 4 per cent of nitrogen. It does not contain more than 2 per cent after its conversion into superphosphate. It is small compared with the 15 to 17 per cent of soluble phosphoric acid which accompanies it. Manure manufacturers, therefore,

increase the percentage of nitrogen by the addition of substances of animal origin. But in Great Britain the manure then ceases by law to be *dissolved bones* and enters the class of *dissolved bone compounds*, and in this latter class the units of nitrogen and phosphoric acid are paid for at a much lower rate than in pure dissolved bones. From a manufacturer's point of view, therefore, it is better to use these nitrogenous adjuncts in making dissolved bone compounds in which little or no bones are used, the bulk if not all of the phosphates being derived from mineral sources. By this means the enormous amount of daily waste from animal sources in large towns can be restored to the soil. The process is as follows: The bones, as they come from the digesters, are mixed still moist with acid of 50° B., and the nitrogenous matter added. These nitrogenous matters are those already studied, but their treatment differs a little from that applied to them when used alone.

Blood.—After coagulating the blood by heat in the manner described later, it is added to the bone dust in the proportion of 300 lb. of fresh blood to 250 lb. of fresh bones. The bone superphosphate thus obtained is rich in nitrogen; it contains in the dry state 4 to 5 per cent of nitrogen, and 9 to 11 per cent of phosphoric acid, and only 0·51 per cent of insoluble phosphoric acid. The bone superphosphate to which blood has been added, dries much better; this latter therefore furnishes a means of obtaining a perfectly soluble powder richer in nitrogen. If it be desired to still further increase the nitrogen and to bring it to 5 or 6 per cent, for example, the difference can be made good by an addition of dried blood, meat meal, or an ammoniacal salt. The addition of so much blood would cause this manure in Great Britain to fall into the class of blood manures; at any rate, a manure with only 9 to 11 per cent of phosphoric acid (say 20 per cent of soluble phosphates), and no insoluble phosphates, would never pass muster as a genuine dissolved bone. All these animal substances the British manufacturer combines with mineral superphosphate and sells as dissolved bone compound, or in this case possibly as blood manure.

Horn.—Although horn previously steamed may be easily crushed in the flatstone mill, it is better to add it in the state of flour to the finished superphosphate, because if added before grinding it does not distribute itself so well as blood. Wool dust and analogous waste are preferably treated like leather waste, for they are too bulky to be treated by steam.

Leather Waste.—It has already been observed that ground leather prepared from tanned leather is one of the least active of nitrogenous manures. They are best treated as follows: The leather is charged into a large leaden pan capable of being heated by a double bottom or by a lead coil, and moistened with sulphuric acid of 50° to 60° B., and the whole heated to boiling. The leather

rapidly dissolves to form a brown liquid, which is drawn off by a tap a little below the false bottom, and which is used in place of ordinary sulphuric acid to dissolve the bones. This method of treating leather presents great advantages. It enables the manufacturer to preserve, in the form of an extract, all the nitrogen, which would otherwise be lost. Besides, and this is an important point, the tannin opposed to the decomposition of the leather in the soil is destroyed. Flesh, lungs, livers, spoilt greaves and other waste are dissolved by the acid in the same way as leather and may be used in a similar manner. Greaves are particularly rich in nitrogen. They often give up as much as 10 per cent of fat to the sulphuric acid used to decompose them. If sulphate of ammonia be used to increase the nitrogen content of dissolved bones, it likewise can be dissolved in the sulphuric acid, whilst nitrate of soda can only be added to the finished product. The mixing is then done by means of the crusher or by the toothed roller mill. Hair, horn, and wool waste are also dissolved by the acid. The solubility of the organic matter is greater in nitrous sulphuric acid than in sulphuric acid alone. For one part of these materials, two parts of nitrous sulphuric acid at 50° or 60° B. should be taken, and if there be no nitrous acid at disposal residual sulphuric acid is fortified by an addition of 2 per cent of nitrate of soda.

Animal Charcoal.—Commercial animal charcoal comes almost exclusively from sugar refiners and glucose factories. To purify their juices, the refiners use large amounts of animal charcoal. In the new state, that is to say, freshly calcined, the black possesses a very energetic decolorizing power. But this property is attenuated by use. To revivify the black, and to restore to it, at least partially, its decolorizing and purifying properties, it is fermented, treated by acids, washed, then again calcined without access of air. Thus revivifying operations give rise to an important waste under the form of a fine powder, which is sold as manure. After a series of revivifications, the granular black is itself spent, revivification being powerless to restore to it its initial properties. Formerly animal charcoal was in current use in sugar works, but within the last fifteen years it has completely disappeared. The refineries alone continue to use it, and consequently it is not so important a manure as formerly. The composition of this product is very variable, according to the methods of manufacture of the sugar refineries. As the char dust (revivification) waste comes always from the surface of the granules of black, and as these parts are the most attacked by the hydrochloric acid used to purify it, it contains an important proportion of carbon, but less phosphate of lime, than the granular black. Moreover, it contains much sand. None the less, it is in much request for the manufacture of superphosphate, because it can be treated without any previous preparation. Spent char contains 25

to 75 per cent of phosphate of lime, 1·5 to 15 per cent of carbonate of lime, and up to 1 per cent of sulphate of lime. Spent char dust contains much less of these substances. As the granular char removes nitrogenous impurities from the saccharine juices, it also contains up to as much as 1 per cent of nitrogen. Some analyses of animal charcoal, both before and after its use in the clarification of syrups, are given in Table LI.

TABLE LI.—ANALYSES OF NEW AND USED AND SPENT BONE CHAR. (PIERRE.)

	Nitrogen. Per cent.	Carbon and Organic Matter (including Nitrogen). Per cent.	Phosphate of Lime. Per cent.	Carbonate of Lime. Per cent.	Various Constituents. Per cent.
Charcoal, fine, new .	1·12	11·6	73·1	8·0	7·3
,, once used	1·95	21·1	64·6	6·4	7·9
Charcoal, fine, new .	1·22	11·3	72·2	5·3	10·5
,, once used	2·83	32·0	53·7	4·9	9·4
,, twice used	3·59	42·2	46·0	3·3	8·5
Charcoal, fine, new .	1·61	11·0	75·6	7·0	13·4
,, once used	2·54	36·2	52·6	10·0	10·1
,, twice used	3·18	42·5	47·5	4·5	5·2

Bone Ash.—The immense prairies of South America support numerous wild herds of cattle; 1000 head of cattle per inhabitant can be counted in many of these countries. The animals are slaughtered for their horns, their skins, and their fat, the flesh being rarely utilized for human food. It is left to rot, or usually becomes food for wild animals. The bones are dried and used as domestic fuel and also in the tallow smelteries, sugar factories, etc., for other fuel is scarce in these districts. It was thus that 100 to 200 years ago hillocks of bone ash had accumulated near dwellings for which, till a short time ago, no use whatever had been found. But owing to the enormous extension of the use of chemical manures, the value of these ashes has been fully appreciated. They are sold to outward bound ships, who purchase them as ballast. As they are in the pulverulent state, bones are also mixed with them, as by doing this they are rendered less cumbersome.

The pressing demand for this excellent waste by chemical manure factories has largely diminished the stocks; on the other hand, bones are now utilized to better purpose, the result being that bone ash has almost disappeared from the market. Five samples of bone ash analysed by Voelcker had the following composition:—

TABLE LII.—SHOWING THE COMPOSITION OF FIVE SAMPLES OF BONE ASH. (VOELCKER.)

	I. Per cent.	II. Per cent.	III. Per cent.	IV. Per cent.	V. Per cent.
Water	4·83	9·91	15·34	3·39	10·30
Organic matter	4·06	1·75	2·03		
Phosphoric acid	35·38	33·89	32·63	38·12	29·56
Lime	41·27	39·53	37·84	44·47	34·48
Lime not combined with phosphoric acid	3·53	3·47	1·92	4·45	1·02
Magnesia	0·97	0·97	1·48	5·67	4·40
Alkalis	—	1·39	0·84		
Oxide of iron and silica	3·01	0·78	0·21		
Carbonic acid			0·84		
Sulphuric acid			0·37		
Sand	6·95	8·31	6·50	3·90	20·24
	100·00	100·00	100·00	100·00	100·00
Phosphate of lime	76·65	73·42	70·47	82·59	64·01

By picking out the big lumps, which consist of almost pure bone ash, a product containing about 85 per cent of phosphate of lime is obtained. The fine powder which contains almost all the sand is, naturally, less rich in phosphate. Bone ash is chiefly used for making precipitated phosphate of lime, according to the method described below. It is worth about £3 per ton.

Bone ash is very hard and difficult to grind, besides it is always wet by absorption of moisture apparently from the air, and is best dried on the engine steam boilers, over which for the time being it acts as a non-conducting composition. Bone ash yields an excellent superphosphate with about 40 per cent of soluble phosphate and 1 per cent of insoluble. It is sometimes a little difficult to dry, but it does so readily in the kiln. The manure manufacturer keenly feels the want of supplies of this most valuable product. An inexpensive machine that would burn spent char to bone ash cheaply and rapidly would supply a great want and enable spent char to fill the place of bone ash, which it cannot now do, as its colour debars it. Bone ash superphosphate, it is needless to say, never retrogrades.

Manufacture of Precipitated Phosphate of Lime.—Precipitated or basic phosphate of lime is a by-product of the manufacture of glue. If hydrochloric acid be poured on fat-extracted bones, it dissolves the phosphate contained therein. An acid solution is then obtained of phosphate of lime, and as a residue the nitrogenous matter, ossein, which is converted into gelatine and dissolved

by boiling with water. Formerly, the acid solution of phosphate of lime was not considered of any value, and to get rid of it, no better outlet could be found than to run it into the river. But now the phosphate of lime is recovered by precipitating it from solution by caustic lime. Unfortunately, the manufacturers are not sufficiently careful in working; the phosphate of lime which they put on the market often containing 12 to 15 per cent of carbonate of lime, or of caustic lime, and a large proportion of calcium chloride, which render it less fit for manure manufacture. The analysis of one of these products furnished the following results:—

TABLE LIII.—ANALYSIS OF PRECIPITATED PHOSPHATE OF LIME.

	Per cent.	
Water and organic matter	26·20	of which nitrogen, 2·68 per cent.
Phosphate of lime	53·50	phosphoric acid, 28 per cent.
Phosphate of magnesia	2·17	
Phosphate of iron	5·30	
Sulphate of lime	2·07	
Carbonate of lime	0·88	
Chloride of calcium	3·50	
Lime	0·46	
Potash	0·21	
Soda	0·29	
Insoluble	5·42	
	100·00	

The material from which this was made was certainly not pure bones, but lately the manufacture of phosphate of lime in glue factories has been perceptibly improved, and the product put on the market is of better quality. Precipitated phosphate of lime is also made from phosphates unfit for converting into superphosphates, and from bone ash, but in the former case the impurities contained in the raw material, such as oxide of iron and alumina, are likewise dissolved, and remain in the product.

The manufacture of precipitated phosphate of lime consists, as already mentioned, in decomposing phosphate of lime by hydrochloric acid, and in separating the chloride of calcium after the equation—

$$Ca_3(PO_4)_2 + 2HCl = 2CaHPO_4 + CaCl_2$$

The phosphoric acid is precipitated from its solution by milk of lime. The neutralization must be done with care, for it requires but a slight excess of lime to form an insoluble phosphate—one part P_2O_5 requires 0·4 of CaO, as the following equations show:—

$$CaH_4(PO_4)_2H_2O + CaO + H_2O = Ca_2H_2(PO_4)_2 2H_2O$$
$$CaH_4(PO_4)_2H_2O + 2CaO = Ca_3(PO_4)_2 + 3H_2O$$

To prepare the acid phosphoric solutions, a wooden vat is fitted with a mechanical agitator, also of wood. No mechanical agitator is, however, required working only with bones. The bones are covered completely with an 8 per cent solution of hydrochloric acid, and left in contact for two to three days. All the mineral matter is dissolved, whilst the ossein, a white soft substance, remains undissolved. The benzine fat-extracted bones decompose more easily than steamed bones. The decomposition is ascertained to be finished when a hollow bone placed at the surface as a sample is soft and supple, and shows well the characteristics of swollen ossein. The solution is then run off through a tap in the bottom of the vat, the ossein is washed with the smallest possible amount of 4 per cent hydrochloric acid, and the liquid is collected in a tank. The wash water is used afterwards to dilute the strong hydrochloric acid, that is why a more methodical extraction is not pursued. As to the quantity of hydrochloric acid, a little more than the theo-

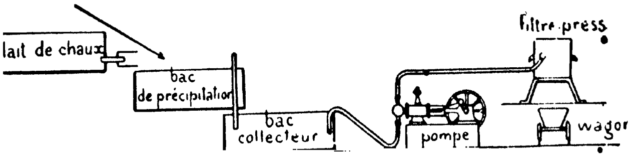


FIG. 37.—Plant for Manufacture of Precipitated Phosphate of Lime.
Lait de chaux = Milk of Lime. *Bac de précipitation* = Precipitation Vat. *Bac collecteur* = Collecting Vat. *Pompe* = Pump.

retical quantity calculated on the lime must be used. When the phosphate is finally ground, solution is effected in ten to fifteen minutes; it is pumped into a filter press by means of a pump with lead lining. The phosphatic solution is collected in an open lead-lined vat, not too deep, in which it is neutralized by milk of lime. To precipitate the $Ca_2H_2(PO_4)_2$ milk of lime is added in quantity just sufficient to neutralize the free HCl, the HCl used, and the phosphoric acid content of the substance being known, then one molecule of CaO is added for each molecule of $CaH_4P_2O_8$. For this purpose there is installed on a level with the top of the neutralizing vat a second lead-lined vat fitted with a tap 15 cm. above the bottom, in which a milk of lime is prepared, which is run into the neutralizing vat, care being taken to stir the mixture in the latter. To make sure that enough milk of lime has been added, a sample is filtered from time to time, and tested with molybdate, or phenol phthalein if the product required is $Ca_3P_2O_8$. To work in a continuous fashion, two neutralizing vats are installed below the milk of lime vat; the latter is then fitted with two delivery pipes,

which are closed when needed by a cork stopper. When the contents of one of the vats is being neutralized, the second is being filled with phosphate solution from the filter press. If excess of milk of lime be added, it is easy to remedy it by running in phosphate solution from the other vat. Finally, there is installed below the neutralizing vats a pit or collecting vat into which the neutralized solution runs through a pipe fixed in the bottom of each of the two above-mentioned vats. To neutralize the solution as exactly as possible, a milk of lime of 15° B. = about 16 per cent CaO is used, of which enough is added to leave the solution just faintly acid; when the liquid is clarified it is decanted from the precipitate, and the neutralization finished apart. The first precipitate is $Ca_2H_2(PO_4)_2$, the second is partly $Ca_3(PO_4)_2$. From the collecting vat the neutralized material is drawn by a suction and propelling pump and forced into a washing filter press in which the precipitate is freed from adherent calcium chloride by washing with water, followed by steaming. The precipitate is readily removed from the liquid. The cakes extracted from the filter press are dried at a maximum temperature of 60° C. (140° F.) best in the steam drying machine.

They are converted into a fine friable powder containing 30 to 40 per cent of P_2O_5. At a higher temperature the $Ca_2H_2(PO_4)_2$ becomes slightly insoluble owing to formation of $Ca_2P_2O_7$. When local facilities lend themselves to it, the vats are installed in such a fashion that the liquid can run from one to the other. The last filter press for the precipitate is then at a sufficient height for the cakes to fall directly into a truck, which conveys them to the drier. The precipitated phosphate is soluble in a solution of citric acid. The manufacture of this product has been the object of numerous researches and several patents.

A precipitated phosphate manufactory requires :—

1 ball mill.
2 agitating vats.
10 filter presses of 250 litres (55 gallons).
5 pumps.
2 lime vats with stirrers.
2 collecting vats.
1 steam dryer.
4 pits with agitators, 2 metres × $2\frac{1}{2}$ metres.

CHAPTER XI.

MANUFACTURE OF BASIC SLAG.

A Retrospective Glance.—In the early days of the application of the Thomas and Gilchrist process, the basic slag from the dephosphorization formed large heaps for which there appeared to be no use. Gradually the idea was evolved that it might be used as a manure, but agronomists did not at first strike upon the true method of utilizing this waste. They imagined, by analogy, that, as with mineral phosphates, it would be necessary to submit it to a similar conversion to the latter. But looking to the nature of the slag itself, one would not dream of converting it into superphosphate. Precipitated phosphate of lime was therefore made from it by Scheibler's patent, which was put on the market as *Thomas' precipitate*, either alone or mixed with nitrate or sulphate of ammonia. This precipitate, prepared by the Fertilitas Company, tested 32 to 35 per cent of phosphoric acid, of which 80 to 90 per cent was soluble in citrate. In May, 1885, The Anglo-Continental Co. took up the sale of the new product, but in spite of the support of this powerful company, Thomas' precipitate did not prove to be a great success, more especially because of its high price. At the same time, G. Hoyermann and Heinrich Albert commenced researches to determine the fertilizing value of the basic slag in its natural state. Hoyermann engaged a certain number of farmers of the province of Hanover to spread finely ground basic slag on marshy lands and meadows. On his part, Heinrich Albert, who had for a long time recognized the solvent rôle of the acids elaborated by the roots of plants, devoted several years to the study of the action exerted on phosphates by weak solvents. He remarked that peat finely ground and kept very moist constituted a somewhat energetic solvent for phosphate. He applied his methods to basic slag and obtained excellent results. In 1885 the agricultural station of Darmstadt took up the matter, and in its turn made cultural experiments with basic slag, thanks especially to the financial support of the syndicate of German manure manufacturers. These experiments were continued for several years, and in 1889 Dr. Paul Wagner published the results obtained. Nevertheless, manure manufacturers themselves remained sceptical, and only two of them consented to deal

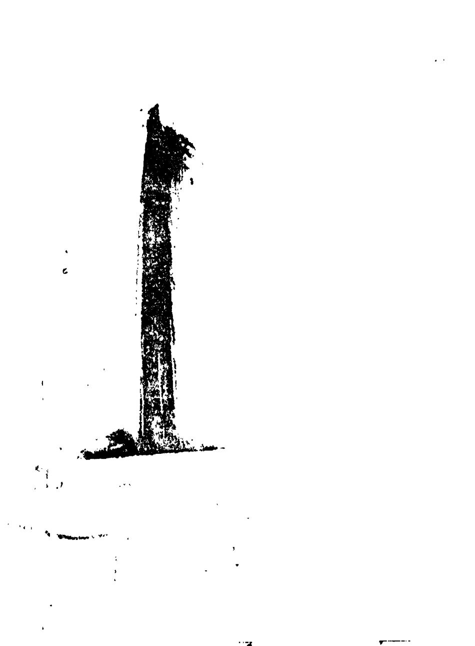
with the metallurgical firms for the supply of basic slag. Their hesitation will be readily understood if one thinks of the great difficulties which they had to surmount, from a technical point of view, in reducing the slag to a fine powder, so as to obtain with a material at that time of very varying strength a uniform marketable product. When, later, the amount of phosphate soluble in citric acid was adopted as a criterion for determining the fertilizing value of basic slag in powder, it was again Hoyermann who, working from his own data, suggested the addition of silica in the converter,

A Steel-Works and its Blast Furnaces.

as a means of considerably increasing the solubility of the phosphoric acid. It is thus that, in spite of apparently insurmountable difficulties, basic slag became a precious source of phosphoric acid for agriculture. Its comparative cheapness, its content of lime and silica, and the good results which they give on meadows, peaty soils, and sandy soils poor in lime, have caused basic slag to be used in all countries in which intensive cultivation is practised. It no longer forms, as previously, a useless and cumbersome ballast, but a product of great fertilizing value, the consumption of which increases year by year.

Origin of Basic Slag.—Up to a comparatively recent epoch, good

steel could be obtained only by using ores either free or almost free from phosphorus, a proportion of 0·25 of phosphorus sufficing to render the iron brittle in the cold. These pure ores became more and more rare, whilst there existed abundant deposits of ore which contained a higher percentage of phosphorus. The attention of metallurgists was, therefore, bound to turn in the direction of the latter, and it was necessary to try to utilize them.



Pouring the Basic Slag from the Thomas Converter into the Removal Wagon.

It is to a young Englishman, Sidney Gilchrist Thomas, to whom in 1879 the honour of this discovery, which afterwards revolutionized the manufacture of steel, is due. It did not enter into ordinary practice until after five or six years of efforts, varied tentatives and numerous and delicate trials. It is now the basis of the manufacture of the greater part of steel. The Gilchrist Thomas process, as it is called, has a double advantage: it enables an excellent steel

free from phosphorus to be obtained whilst utilizing the phosphoric ore; and, on the other hand, it gives as a secondary product a fertilizing material, the use of which, in agriculture, has assumed a rapid and considerable extension. Let us now examine briefly the manufacture of the cast-iron, then that of the steel which yields the slag. The ore conveyed to the irónworks is smelted in blast furnaces which are about 65 feet in height by 20 feet in width; it is there laid alternately with layers of coke, and there is added, according to the nature of the mineral, calcareous or silicious matter which forms what is called the flux. The object of this fluxing is to deprive the mineral of any argillaceous or calcareous gangue present, and to obtain finally, in consequence of the de-oxidation and of the partial carburation of the ore, as a useful product cast-iron, and as residue a lighter substance floating on the top constituting the slag, which contains the major part of the impurities combined with the materials of the flux.

As to the gases which escape in consequence of this de-oxidation they are collected and their heat utilized, partly to heat the air which enters the blast furnaces to a temperature of 750° C., and to produce the steam necessary to drive the blowing engine, or finally to produce electricity. The charging of the blast furnace is done about every six hours through the top; there is a discharge of slag and iron through the bottom. The temperature of the lower zone where the molten iron frees itself by difference of density from its floating impurities is about 1200° C. The slag is utilized industrially for making bricks, cement, etc. Let us see what becomes of the cast-iron, which at this point is still phosphuretted, as the following analysis taken as an example shows:—

TABLE LIV.—ANALYSIS OF CAST-IRON SHOWING PHOSPHORUS CONTENT.

	Per cent.
Iron	91·20
Carbon	3·60
Phosphorus	2·75
Magnesia	3·20
Silicon	0·25
	100·00

The conversion of the cast-iron into steel is brought about in special pear-shaped vessels movable round a horizontal axis, and constructed of steel plates lined with refractory stone. These appliances, termed converters, are, in the Thomas process, lined in the interior with lime and magnesia. They are open at the top and pierced in the lower part by holes through which air at a high temperature can be blown. To charge them they are turned upon their axes to

an angle of 90° and the liquid cast-iron is run in through the upper opening. Then the converter is raised at the same time that air is driven through the lower holes at a sufficient pressure for the fused metal to remain in the converter and not pass through the holes. Under the influence of the high temperature prevailing in the converter, and of the air injected, the silicon, the sulphur and the phosphorus are burnt at the same time as a part of the carbon. The heat which is disengaged inside the converter is such that the metal which had at the moment of its introduction a

Unloading Basic Slag in Blocks.

temperature of 1200°, rises to 2100°, all within thirteen minutes. The phosphorus is oxidized and is converted into ortho-phosphoric acid, and as it is in the presence of excess of lime, it combines in a peculiar form—tetrabasic phosphate—associated with calcium silicate, forming what is known as basic slag. When the operation is finished, which is ascertained by the appearance of the gas given off from the top of the converter, the latter is inclined on its axis, the current of air is suspended and the liquid slag floating on the cast-iron is poured into a metallic truck forming a case and containing a certain quantity of finely pulverized fused silica. The weight of the slag in one of these trucks may amount to 4½ tons

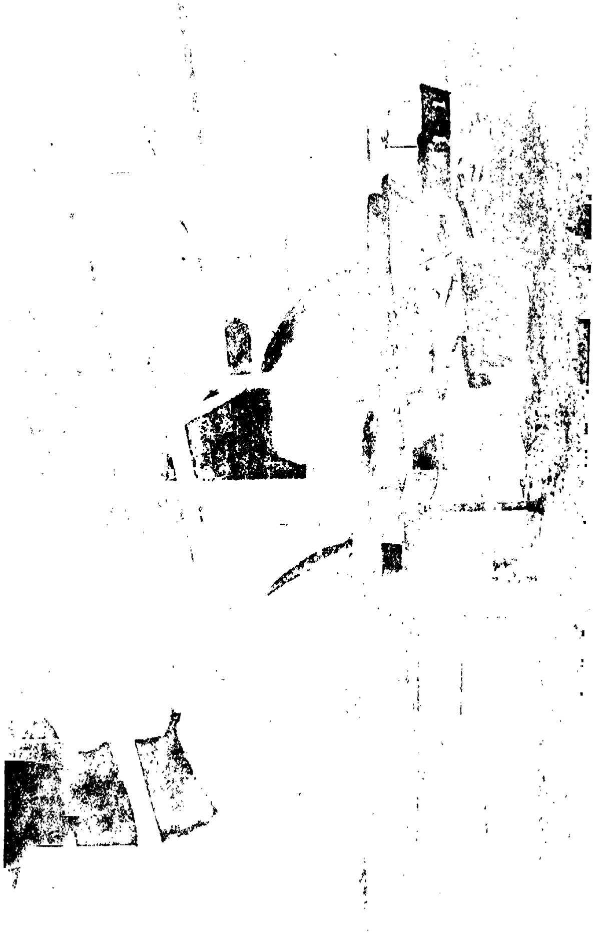
and even more. The whole is conveyed on rails to the spot where it is to be handled, and after cooling, facilitated by sprinkling with water, the mass is removed from the truck and discharged into a crushing shed.

The Nature of Basic Slag.—Basic Slag occurs as more or less bulky blackish fragments, porous, strewn with pellets of steel and of great density. It slakes in the air; the caustic lime absorbing moisture and carbonic acid and the ferrous oxide oxidizing. Contrary to an opinion expressed at first, the absorption of carbonic

Preliminary Breaking-up of Basic Slag.

acid decomposes the tetrabasic phosphate. In the porous part of the slag translucent crystals are met with, rhombic tablets, hexagonal prisms, and monoclinic needles 10 to 15 mm. long, of a grey, brown, or blue (produced by FeO) colour intermingled or ranged symmetrically. These crystals consist principally of tetrabasic phosphate of lime, $Ca_4P_2O_9$. They have been the object of very interesting researches, the principal points of which will now be summarized.

Tetraphosphate of Calcium.—$Ca_4P_2O_9$ may be regarded as being the neutral salt of an octobasic diphosphoric acid, $P_2O(OH)_8$, not yet produced in the free state, the structural formula of which would be the following :—



Thomas Converter at work.

$$O\left\{\begin{array}{l}P\left\{\begin{array}{l}OH\\OH\\OH\\OH\end{array}\right.\\P\left\{\begin{array}{l}OH\\OH\\OH\\OH\end{array}\right.\end{array}\right.$$ and that of the corresponding tetra calcic phosphate $$O\left\{\begin{array}{l}P\left\{\begin{array}{l}{O \atop O}>Ca\\{O \atop O}>Ca\end{array}\right.\\P\left\{\begin{array}{l}{O \atop O}>Ca\\{O \atop O}>Ca\end{array}\right.\end{array}\right.$$

The presence of this compound in basic slag has been determined by a great number of scientists, so that there can be no doubt as to the soundness of the hypothesis enunciated above. The small blue crystals which are found in the paste, and more especially in the *geodes* of the slag, were studied from a crystallographic point of view by A. Richard, who refers them to the orthorhombic system, and notes amongst their properties a strong double refraction and a very marked dichroism, the same crystal appearing colourless or a beautiful cobalt blue in opposite positions. Prof. Carnot at this time termed these crystals silico phosphates of lime and gave them the formula $P_2O_5SiO_25CaO$. In the same year Hilgenstock examined the other crystals. He found in the scoriæ of the slag, crystals in the form of thin rectangular tablets colourless or of a light brown tint according to the thickness. He placed these in the rhombic system, and recognized their composition as that of a tetrabasic phosphate of lime, $Ca_4P_2O_9$ or P_2O_54CaO. This analysis, having given rise to a certain amount of discussion, it was again taken up by Carnot on the one hand and on the other by Stead and Ridsdale. They found :—

TABLE LV.—ANALYSES OF CRYSTALS OF TETRABASIC PHOSPHATE OF LIME FOUND IN BASIC SLAG.

	Carnot. *Per cent.*	*Stead and Ridsdale.* *Per cent.*
Phosphoric acid	37·67	38·044
Silica	0·74	traces
Lime	59·54	60·206
Magnesia	traces	0·82[illegible]
Ferrous oxide	1·44	0·100
Alumina	0·37	
Vanadium oxide	—	0·722
Sulphur	—	0·150
	99·76	100·050

These results confirm the formula of tetrabasic phosphate of lime, besides the two forms of crystals described. There were likewise found brown or almost colourless needles of a hexagonal form. Analyses of these give the following figures :—

TABLE LVI.—ANALYSES OF HEXAGONAL CRYSTALS FOUND IN BASIC SLAG.

	Hilgenstock. Per cent.	Bucking and Link. Per cent.	Head. Per cent.
Phosphoric acid	34·94	36·77	33·707
Silica	3·24	3·81	3·900
Lime	57·55	53·51	53·536
Magnesia	—	0·40	0·486
Manganous oxide	—	—	0·790
Ferrous oxide	4·00	2·22	1·286
Ferric oxide	—	1·78	4·857
Alumina	—	1·09	—
Vanadium oxide	—	—	1·343
Sulphur	—	traces	0·460
	99·73	99·58	100·365

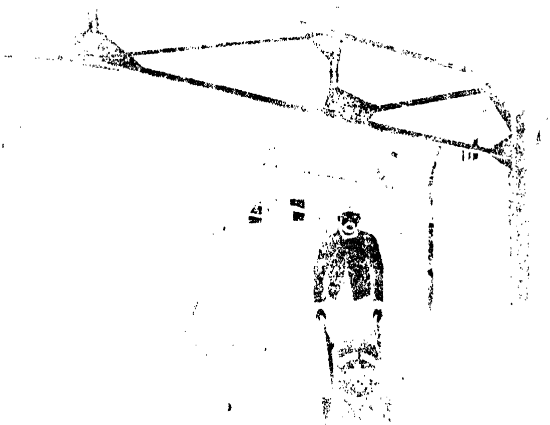
Feeding Basic Slag into Ball Mills. (View from above.)

The differences which exist between these analyses are explained by the difficulty experienced in isolating the crystals from the impurities which remain partially adherent thereto. Stead and Ridsdale have in fact distinguished two other varieties of crystals, flat black

needles, some of which are magnetic, while the others are not so. They have found the composition to be as follows:—

TABLE LVII.—ANALYSES OF BLACK NEEDLES, MAGNETIC AND NON-MAGNETIC, FOUND IN BASIC SLAG.

	Magnetic.	*Non-magnetic.*
Lime	39·088	44·730
Magnesia	1·297	0·936
Alumina	6·400	9·700
Ferric oxide	33·857	35·657
Ferrous oxide	8·100	—
Manganous oxide	1·748	1·023
Chromium sesquioxide	5·980	4·200
Vanadium oxide	2·656	2·223
Silica	1·100	0·900
Phosphoric acid	traces	0·740
	99·826	100·109



Handling of Ground Basic Slag. (Bagging-up in 100 kilos (220 lb.) lead-sealed bags.)

According to these authors, these crystals would therefore consist chiefly of ferrite and of aluminate of lime. The analyses of the blue crystals give:—

TABLE LVIII.—ANALYSES OF BLUE CRYSTALS FOUND IN BASIC SLAG.

	Carnot. Per cent.	Hilgenstock. Per cent.	Bucking and Link. Per cent.
Phosphoric acid	29·65	30·85	31·19
Silica	12·42	9·42	9·47
Lime	53·20	57·60	57·42
Magnesia	traces	—	traces
Ferrous oxide	1·80	2·94	0·95
Manganous oxide	traces	—	—
Alumina	2·76	—	1·13
Sulphur	—	—	traces
	99·83	100·81	100·16

These figures correspond exactly with the formula—

$$8P_2O_5, 8SiO_2, 36CaO, FeO, Al_2O_3$$

By replacing small quantities of oxide of iron and alumina by equivalent amounts of lime, a more simple formula is arrived at, P_2O_5, $SiO_2 5$, CaO, which may also be written—

$$P_2O_5, 3CaO + SiO_2, 2CaO$$

Hilgenstock and Carnot have examined the order of formation of the crystals, and both have come to the same conclusions.

The first crystals which are formed appear to be the rectangular tablets on which afterwards come the brown hexagonal needles. It is only later that the rest of the slag, becoming richer in silica, isolates the blue and brilliant crystals. These are superposed by the brown and black needles. The order of appearance seems, therefore, regulated both by the gradually decreasing temperature and by the composition of the bath of slag which becomes richer in silica and less rich in phosphoric acid. Cultural experiments have been made with the object of examining the action of certain elements of basic slag. These will be examined subsequently.

Solubility of Basic Slag.—Formerly basic slag was regarded as a product of no value, because there was no suitable means of dissolving it, owing to its high percentage of iron and lime; neither was any attempt made of utilizing it in agriculture, because it was very well known that raw phosphates possess no direct fertilizing value. Scheibler suggested the preparation from the basic slag of a precipitate (German patents 24,130 and 25,020). For that purpose he treated 100 parts of basic slag in powder with 120 to 150 parts of hydrochloric acid and precipitated the phosphoric acid by milk of lime. Francke recommended the decomposition of basic

slag by magnesium chloride (German patent 27,106), converting the phosphoric acid into phosphate of magnesia. G. Meyer, on his part, suggested the treatment of fused basic slag with its own weight of acid sulphate of potash. The silicate of potash ought to give still better results. The object of all these treatments was to facilitate grinding on the one hand, and on the other to increase the fertilizing value of the basic slag, by dissolving it. But up till now no steel-works has felt it advisable to resort to these mixtures, in order to improve the manipulations which they suppose in no way hinder the progress of the manufacture. The last-mentioned process would, however, appear to have the advantage of suppressing the unpleasant element which the spreading of basic slag now presents. None of the processes which have been suggested to increase the fertilizing value of this manure need be dwelt upon here, since they have not been adopted in actual practice. It was first of all asserted that the phosphoric acid of basic slag, owing to its origin, was less soluble than that of the ordinary form, but V. Reis and Arens, amongst others, showed that phosphoric acid combined with the silicate of lime was soluble in carbonated water. It is from these researches that the use of basic slag in agriculture dates. The results obtained by these two are given in the following table (p. 212); the figures of this table showing the great solubility of basic slag in water saturated with carbonic acid compared with that of the other phosphates. The decomposition of tetraphosphate of lime takes place according to the equation—

$$P_2O_9Ca_4 + 6CO_2 + 5H_2O = CaH_4(PO_4)_2 + 3CaH_2(CO_3)_2$$

There is thus formed an acid phosphate of lime such as is also found in superphosphates. The solubility of basic slag in citric acid and in citrate of ammonia and also in tartaric, acetic, and oxalic acids has been the subject of profound researches by E. Jensch which are of so much the greater interest because the solubility in the same solvents of the calcareous silicates always present in basic slag were determined at the same time. Jensch's researches were made on basic slags of very different ages and origins for comparison. He determined also the solubility of both Podolia phosphorites and Somme phosphate. The method pursued consisted in mixing in each case 1 grm. of the substance with 150 c.c. of the solvent concentration 1 in 20, exposing the mixture during twelve hours to a temperature of 50° to 70° C., then diluting the solution in 100 c.c. of water. The liquid was heated to boiling, filtered to separate the insoluble matter ignited, and the phosphoric acid titrated in the usual way. The difference in the contents of the different elements in the residue, on the one hand, and the raw material, on the other hand, gives the quantities dissolved by the organic acid. Jensch operated on eleven samples of basic slag reduced to a fine powder

(1 to 11); three samples of crystals of raw slag (12, 13, 14). A sample of Podolian phosphorite (15) and a sample of Somme phosphate (16). The following table (p. 213) gives, on the one hand, the proportion of silica, lime, and phosphoric acid, on the other hand, the quantities of phosphoric acid dissolved by the different solvents, also the amounts remaining undissolved in the residues. These figures show that the phosphoric acid behaves in the same manner in basic slags containing more than 18 per cent of that acid as in those which only contain it in small proportion. Thus it is that rich basic slags in current use in agriculture only contain 0·13 to 0·20 insoluble in citric acid, whilst low strength basic slags only contain 0·04 to 0·14 per cent. The solubility in oxalic acid yields equally concordant results. That acid dissolves tetracalcic phosphate and only gives a slight residue of insoluble which consists probably of tricalcic phosphate. The crystals separated from the basic slags (12, 13, 14) show a still greater solubility. The other organic acids used in this series of experiments act less energetically on the phosphates of basic slag; however, here again a certain uniformity can be established between the solubility of the different phosphates.

The silicates, which are highly basic, although of a composition often very variable even when of the same origin, are distinguished by their solubility in the organic acids, a property which is absolutely wanting in the silicate compounds of the natural phosphates, phosphorite, apatite, etc. It follows that the degree of solubility of the phosphoric acid of basic slag depends on the nature of the calcareous silicates contained therein. Again, if the fragments of basic slags show a uniform crystalline structure, that is to say, if they are deprived of agglomerations of caustic lime, which are sometimes observed therein, their content in free lime will be very small and will rarely exceed 2 per cent. But the more these calcareous agglomerates are present, the higher will be the free lime content. It is true that this lime, not being combined chemically with the phosphate, but in a state of simple mixture, and up to a certain point as impurity, cannot exercise any influence on the solubility of the phosphoric acid in the soil, for those bodies can only act as solvents which are of a nature to modify the chemical nature of another body. The neglect of this principle has led some authorities to ascribe to the uncombined lime in basic slag an importance which it absolutely does not possess. What determines the solubility of the phosphoric acid in basic slag is the strongly basic calcareous silicates with which it is combined.

The magnesia likewise forms with the phosphoric acid a tetraphosphate, but the solubility of this body considerably exceeds the solubility of the corresponding calcareous compounds. Basic slags rich in magnesia dissolve much more rapidly in organic acids than

TABLE LIX.—SOLUBILITY OF BASIC SLAG IN WATER SATURATED WITH CARBONIC ACID.

	Content of			Quantities dissolved by 10 litres of water saturated by CO_2			Comparative Solubility.		
	SiO_2 Per cent.	P_2O_5 Per cent.	CaO Per cent.	SiO_2 Per cent.	P_2O_5 Per cent.	CaO Per cent.	SiO_2 Per cent.	P_2O_5 Per cent.	CaO Per cent.
Basic slag I.	2·57	18·30	48·68	1·51	4·19	19·37	58·8	22·9	39·8
,, II.	5·20	15·07	48·82	3·15	5·66	24·84	60·6	37·6	50·9
,, III.	2·85	21·30	48·36	2·11	7·55	27·85	74·0	35·5	57·5
,, IV.	4·05	18·33	50·35	2·27	6·81	24·19	56·7	37·1	48·0
,, V.	7·67	16·32	47·98	4·22	7·89	24·54	56·0	48·3	51·1
,, VI.	6·93	15·74	48·15	3·55	4·50	25·08	51·2	28·7	52·0
,, VII.	5·54	24·00	46·35	3·05	7·59	19·36	55·0	31·6	41·7
Shell slag	18·15	13·47	44·10	4·99	3·45	15·17	27·4	25·5	34·4
Prepared slag	6·58	24·95	51·25	4·07	7·79	21·00	61·8	31·2	40·9
Scheibler's precipitate	8·02	33·36	31·10	0·62	7·36	9·37	7·7	22·0	30·1
Hoyermann's precipitate	5·70	14·93	34·05	1·29	4·96	19·96	22·7	33·0	58·5
Bicalcic phosphate of lime	—	51·09	41·03	—	8·57	6·95	—	16·8	16·8
Tricalcic phosphate of lime	—	43·26	51·45	—	5·41	7·04	—	12·5	13·6
Tetracalcic phosphate of lime	—	36·85	62·70	—	15·52	33·27	—	42·1	53·0
Degreased cattle bones	—	25·23	32·75	—	7·19	9·65	—	28·5	29·5
Bone ash made from above bones	—	41·71	55·75	—	2·29	3·29	—	5·5	5·9
Phosphorite	1·77	32·00	45·36	0·10	1·00	1·67	5·7	3·1	3·7

TABLE LX.—SHOWING THE RESULTS OF JENSCH'S RESEARCHES ON BASIC SLAG.

	Commercial Basic Slags.										Crystals.				Phosphorites.	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Silica	4·41	5·03	10·04	14·15	22·41	10·08	20·77	6·94	19·49	8·98	9·39	2·24	12·14	3·58	2·18	3·61
Lime	54·17	56·03	49·1	48·83	40·04	49·45	39·71	48·07	42·25	44·02	48·63	60·10	62·62	60·81	48·67	50·22
Phosphoric acid	18·21	19·64	18·03	16·26	13·23	16·86	12·41	40·32	16·28	14·83	15·18	36·40	24·81	27·10	38·20	35·29
Of which soluble in :—																
(a) Citric acid	18·08	19·60	17·98	16·24	13·15	16·78	12·32	20·30	16·22	14·80	15·04	36·39	24·77	27·08	0·16	0·2
(b) Tartaric acid	3·96	4·27	3·91	3·84	2·22	3·63	3·02	6·41	2·87	2·45	2·23	6·49	5·06	5·97	0·02	0·03
(c) Acetic acid	5·33	6·21	4·11	4·37	2·46	3·88	3·10	8·12	3·07	2·06	2·64	18·80	17·32	9·17	—	trace
(d) Oxalic acid	18·11	19·52	17·94	16·05	13·06	16·70	12·23	20·06	16·20	14·73	15·06	36·37	24·80	27·03	trace	—
(e) Neutral ammonium citrate	3·78	3·24	4·09	3·66	1·88	4·01	2·97	[illegible]·14	2·90	2·65	3·02	16·72	16·24	5·83	—	—
Insoluble per cent of total phosphoric acid (a)	0·71	0·20	0·27	0·12	0·60	0·48	0·73	0·50	0·37	0·20	0·92	0·03	0·16	·07	99·58	99·45
(b)	78·25	78·26	78·30	76·38	83·22	78·47	75·66	84·10	82·37	83·48	85·33	82·17	79·60	77·97	99·95	99·92
(c)	70·73	68·37	77·20	73·12	81·41	77·00	75·02	79·87	81·14	86·10	82·62	48·35	30·19	66·16	—	—
(d)	0·55	0·61	0·50	1·28	1·28	0·95	1·45	50·25	0·49	0·68	0·79	0·08	0·04	0·25	—	—
(e)	79·24	83·49	77·36	77·48	85·79	76·21	76·07	92·21	82·21	82·13	80·10	54·07	34·54	78·49	—	—

those in which magnesia is absent. The action of citric acid on the slags shows that the magnesia is chiefly combined with the phosphoric acid and not with the silica. It is perfectly possible, and in all cases very likely, that the action of phosphoric acid of basic slag in the soil depends, in the first instance, on the presence of these silicates. We would thus be confronted with double compounds, phosphates, and silicates of calcium which are dissolved with the greatest facility by water containing carbonic acid, hence, therefore, the solution of the phosphoric acid and its absorption by plants follows. It has been remarked, in fact, that the most active basic slags are always those with a high percentage of silica. Steel-works, therefore, possess a very simple and in no way costly method of increasing the solubility of basic slag in citrate; it suffices to add hot sand to it in the converter: the sand melts like butter, is converted into silicic acid and combines with the phosphate of lime to increase its solubility. It is clear, in that case, that lime should not be deficient in the slag. Silica, therefore, plays a very important rôle in the basic slag. Ca_2SiO_4 converts the slightly soluble phosphate of the slag into $Ca_4P_2O_9$ according to the following equations:—

$$Ca_3(PO_4)_2 + Ca_2SiO_4 = Ca_4P_2O_9 + CaSiO_3$$
$$Fe_3(PO_4)_2 + 2Ca_2SiO_4 = Ca_4P_2O_9 + Fe_3Si_2O_7$$

The introduction of an excess of silica also helps to decompose $Ca_4P_2O_9$. There exists in Germany a factory which makes basic slag with ·24 per cent of phosphoric acid according to Scheibler's patent (German patents 34,416 and 41,303). A little less lime than that required for the complete dephosphorization of the cast-iron is added to the converter, and the slag so obtained run out. The remainder of the lime is then added, and the low strength slag which results is used as a reducing substance in the converter. To increase the strength of the slag in phosphoric acid, phosphatic chalk may also be added to the cast-iron in lieu of lime, eventually mixed with sand. Fused phosphatic chalk has the same solubility as the best slags. ($CaCO_3$ melts at 1000° C., the phosphate at 1900° C.)

Crushing of Basic Slag.—In the beginning of the basic slag industry the material was found very difficult to crush. Cylindrical crushers and flatstone mills were used at that time. But as the basic slag is mixed with grains of steel of larger or smaller size, the plant became rapidly worn out. Attempts were then made to eliminate the pieces of iron in the basic slag by means of magnetic separators. But these methods did not give good results; the separation of iron was incomplete and the cleaning of the machines involved frequent stoppage. From 1888 mills with forged steel balls, the wear of which is very slight, have been used. Ball mills, moreover, almost entirely do away with dust, owing to the installation of a special chamber intended to collect it, and of a draught

chimney which draws it thereto. The hot air entering the draught chimney contains the dust formed in the crusher; about 1 per cent of dust being produced for 100 of fine powder. When fans were used—previous to the present system—6 per cent of dust was obtained. The dust chamber is emptied every eight to fifteen days, according as the work is by day or continuous day and night. The blocks of basic slag are first broken up by hand to eliminate pieces of iron, which are laid on one side to return to the foundry. The basic slag so obtained is then reduced to a fine powder (passing through a 100 sieve) in ball mills. The powder is collected from the lower part of the mill and bagged up in 2 cwt. (220 lb.) bags. Formerly the basic slag was allowed to slake in the air, and the fragments, after eliminating the iron, were ground in flatstone mills. But basic slag, slaked after long exposure to atmospheric agents, sometimes contains excessively hard pieces, resisting the most powerful grinding; for this reason the method was abandoned. The treatment to which the basic slag is subjected as it comes from the converter has a considerable effect on the grinding. V. Reis has examined the composition of basic slag and its relation to its resistance to grinding. From an outward inspection there are two kinds of basic slag, block slag and poured slag. Block basic slag is produced when it is allowed to solidify in the wagons into which it is poured from the converter. It then cools slowly and uniformly, and may be removed in a single block which is easily detached from the platform of the wagon. Poured basic slag is obtained by pouring the contents of the wagon on the ground. It spreads out in a thick layer and cools rapidly. This kind of basic slag is generally very hard; grinding is difficult and requires a great expenditure of motive power. Basic slags in blocks, on the contrary, are more easily ground, but they also contain very hard lumps. The following table by Reis gives the composition of different slags and their resistance to grinding:—

TABLE LXI.—EFFECT OF COMPOSITION OF BASIC SLAG ON FACILITY OF GRINDING.

	I.	II.	III.	IV.	V.	VI.	VII.
Silica	6·77	16·41	6·69	4·88	8·07	6·00	7·07
Phosphoric acid	16·92	11·75	17·75	19·25	18·48	18·39	22·50
Alumina	1·68	1·58	0·95	0·59	1·40	1·37	0·89
Ferric oxide	0·96	10·41	5·70	5·14	3·45	2·87	5·27
Ferrous oxide	10·77	10·55	10·65	12·49	10·13	11·43	6·49
Lime	51·00	31·00	48·42	48·17	46·47	50·77	47·36
Manganous oxide	7·16	14·91	7·71	6·23	9·35	7·28	7·81
Magnesia	3·01	2·08	2·05	2·38	2·03	1·57	1·67
Crushing	difficult	easy	easy	less easy	difficult	difficult	easy

I. Poured slag, dark brown, hard and difficult to grind.
II. Block slag, grey, lamellar, friable, easily ground.
III. Block slag, slate grey, firm, and easily ground.
IV. Block slag, grey, firm, vesicular, less easily ground.
V. Poured slag, dark brown, hard, brittle, difficult to grind.
VI. Block slag, brown, brittle, hard, difficult to grind.
VII. Block slag, grey, lumpy, difficult to grind.

It follows from these figures that in general the chemical composition of basic slag has only a slight effect on its physical properties, whilst the percentage of oxide of iron would appear to increase their resistance to grinding, as the following table shows:—

TABLE LXII.—SHOWING THE INFLUENCE OF THE RATIO OF THE PEROXIDE OF IRON TO PROTOXIDE ON THE EASE OF GRINDING OF BASIC SLAG.

Basic Slag.	Peroxide of Iron.	Protoxide of Iron.	Ratio of Fe_2O_3 to FeO.	Grinding.
1	0·96	10·77	1 : 11·2	Difficult
2	10·41	10·55	1 : 1·0	easy
3	5·70	10·65	1 : 1·9	,,
4	5·14	12·49	1 : 2·5	less easy
5	3·45	10·13	1 : 3·0	difficult
6	2·87	11·43	1 : 4·0	,,
7	5·27	6·49	1 : 1·2	easy

When the ratio of the peroxide of iron to the protoxide is lower than 1 : 3 the basic slag is generally easily ground, especially when the peroxide of iron is in preponderant proportion, but when the protoxide of iron predominates largely the slags are hard and difficult to grind. It is important to watch the sieves around the crusher, and see that they are working well, so as to be able to remedy any defect forthwith. With this end in view, the basic slag produced each time by four crushers is carried to a weighing machine manipulated by a trustworthy man; the latter registers the production of each crusher, takes a small sample from each bag, which he examines by the feel and the sieve and runs it into a box installed for the purpose, or each chief grinder weighs his product and is himself responsible for the good execution of the work and its bagging up. Then the sacks are carried to the depot. Since in the slack season orders must be executed from stock, it is necessary to use very sound and carefully sewn bags and to preserve them full in a dry place, because ground basic slag, owing to its high lime content, is apt to solidify in a damp place. The moistened powder cakes together and cannot be rendered friable by drying as one might suppose; it only becomes harder. The 2 cwt. bags (220 lb.) measure

50 × 90 cm. (20 × 36 in.). Even in using sound bags some of them rot when stored full. That is why basic slag is stored in iron silos.

It has already been mentioned that the cooling of basic slag is accelerated by quenching with water, an operation which is not without danger. When basic slag, solid on the outside but incandescent within, is exposed to the shower of water, this may penetrate into the interior of the block by cracks and crevices; it is converted into steam which occupies a volume 1300 times greater at 100° C. and 7500 times greater at 1000° C. When such steam is given off instantaneously a very small quantity of water suffices to cause an explosion. It may also happen that a block of basic slag in which the centre portion, still liquid, may escape, will be particularly dangerous for the workmen. It is necessary, therefore, to draw their attention thereto. Finally, gas may form inside the basic slag without exterior aid, which, in virtue of its tension, seeks an outlet, and not finding any, blows the block to pieces. When a crusher has to be repaired, and if the repairs cannot be done on the spot, it is conveyed to the forge on a moving crane or on a truck running on rails. Crushing being a work which requires to be continuous, the machines are not stopped except for dinner at noon, otherwise they work continuously, the workmen replacing each other at lunch time. During the dinner hour the machines are inspected and the bearings lubricated. The grinding plant should be simple. Owing to the peculiar nature of the substance to be ground, conveyers and mechanical feeders are not applicable. A crusher of 2 metres ($6\frac{1}{2}$ feet) can produce 15 tons in 10 hours of ground basic slag, when the basic slag is freshly cooled and not too hard. P. Mellman, of Berlin (German patent 107,234), projects a jet of steam or air into the liquid basic slag at the moment it is discharged by the converter. The basic slag is then blown into a friable mass which is very easily ground. The basic slag in blocks is sold to the grinding factories according to its percentage of phosphoric acid. The determination is generally made on the powder produced during crushing, assuming that the grinders possess covered and very dry warehouses. On the other hand, the vendor takes a sample from each block by chipping off a fragment with the hammer and from the collected chips a fair average sample is taken at the end of each month. The sample is crushed, mixed, and divided into three parts; one part is sent to the buyer, the other to the sender, and the third is sealed and kept in reserve for an independent analysis in case of difference. The exchange of analyses on both sides is made on a certain day, and the average is taken as a basis when the difference between the two analyses does not exceed 0·5 per cent P_2O_5. If the difference be greater, the sample in reserve is sent to an analytical station agreed on by both buyer and seller, and the analysis which it supplies forms

the sole basis of adjustment. The cost of the analysis is borne by the party whose analytical results are furthest from those of the analytical station. If the analytical results on both sides differ to an equal extent from the experimental station, the costs of settlement are defrayed equally by both parties.

Basic slag is delivered to farmers without any admixture with other manures. If it be mixed with potash salts it heats and gradually solidifies, the caustic lime, acting on the magnesium chloride they contain, forming magnesium oxychloride, which is a powerful cement; if mixed with sulphate of ammonia, the caustic lime acts on the salt with consequent loss of ammonia. Finally, if mixed with nitrate, the nitric acid may be reduced to ammonia by the iron which is contained in the slag in the form of a fine powder, and the ammonia expelled by the caustic lime.

Customs in the Sale of Basic Slag.—From 1 July, 1895, according to a decision of the Assembly of German Agriculturists, basic slags were sold on the basis of their phosphoric acid soluble in citrate, without taking into account their total phosphoric acid, nor the degree of fineness.

But in its General Assembly held in 1898, the Union of Experimental Stations decided no longer to use Wagner's citrate of ammonia solution. It, moreover, found that steel-works, to increase the solubility of their basic slag in citrate, were adding to the cast-iron not only silica, but more lime. The effect of this was to increase the alkaline nature of the basic slag, and the Union estimated that this increase in alkalinity justified the selection of a solvent of greater acidity in the estimation of soluble phosphoric acid. The 2 per cent solution of citric acid forms, in fact, a more accurate method than citrate of ammonia for basic slag prepared according to this new process. But Professor Wagner estimates that the 2 per cent citric acid solution dissolves 7 per cent more of the total P_2O_5 in basic slag, that is to say, it shows 16 per cent of soluble phosphoric acid where the old method only showed 15 per cent.

There is at the present time a tendency to value basic slag on the basis of its total phosphoric acid content, a plan which has some justification, judging from the cultural experiments made on the subject by Meissl and Defert in Austria.

Remarks on the Use of Basic Slag.—It is not intended to examine here the effect of basic slag on vegetation; that examination being fully dealt with in a special work just published by the author. The remarks made here will therefore be confined to a few points more immediately connected with the study of basic slag.

Guffroy, an agricultural engineer, having undertaken researches as to whether the silica and the manganese in basic slag had any

fertilizing action, isolated, as completely as possible, the blue crystals (silico-phosphate) and the brown crystals (tetraphosphate), examined above, and caused them to be analysed in Professor Grandeau's laboratory. The following are the results:—

TABLE LXIII.—ANALYSES OF BLUE AND BROWN CRYSTALS IN BASIC SLAG.

	Brown Crystals. Per cent.	*Blue Crystals.* Per cent.
Total phosphoric acid	21·71	20·28
Lime	48·88	51·52
Silica	1·49	5·17
Manganese calculated to the metallic state	2·46	1·86

Trials were then made:—

1. With a basic slag of known composition.

2. With a basic slag presenting the same composition, and of which the phosphoric acid was furnished by crystals of tetraphosphate and silico-phosphate of natural basic slag.

3. With an artificial basic slag in which, by using only tetraphosphate, and in another silico-phosphate, there was formed:—

(*a*) A basic slag deprived of silica.

(*b*) A basic slag containing little manganese.

From the comparison of the results obtained it was easy, consequently, to infer the action of the ingredients, manganese and silica. The first researches were made in collaboration by Guffroy, Milon, and Crepeaux. The results have been summarized by the National Society of Agriculture.[1]

The plants experimented on were buckwheat, wheat, and violet trefoil. From this first series of experiments there was deduced the double efficacy of manganese and silica, in basic slag *Etoile* brand. The second series of experiments, the results of which were not published, were made by Guffroy and Milon alone, on wheat, buckwheat, and hemp; at the same time the violet trefoil of the first experiment was kept under observation. The result of these experiments may be summarized thus:—

1. Apart from its phosphoric acid, lime and magnesia, *Etoile* basic slag has proved efficacious owing to its manganese and silica.

2. Manganese from an agricultural point of view ought to be regarded as an important constituent, influencing both the quantity and the quality of the crop.

3. It seems that silica, at least in the condition in which it exists in *Etoile* basic slag, also acts in the same direction, but that its

[1] "Bullet. de la Soc. National d'Agric., 1905," pp. 479-83: "On the Fertilizing Action of Certain Accessory Products in Basic Slag".

action is weaker, less decided, and requires to be further studied in order to establish without question its beneficial action.

According to the Institute Internationale d'Agriculture, Rome, the production of basic slag in 1910 was as follows:—

	Metric tons.
Germany	2,007,500
France	534,000
Belgium	488,000
United Kingdom	160,000
Austria-Hungary	74,000
Sweden	12,345
	3,275,845

These figures are based on the assumption that 250 kilos of slag are formed per ton of steel produced. As pointed out by Dr. Russell[1] the figures for the United Kingdom are certainly incorrect. According to Professors Gilchrist and Louis[2] the production in this country is 850,000 tons, some of which is of low grade, the percentage of phosphoric acid being about 10; if, however, it is calculated to a basis of high grade quality, i.e. containing 17 to 20 per cent of phosphoric acid, it amounts to 600,000 tons.

[1] "Jour. Soc. Chem. Indt.," 1917, p. 252. [2] *Ibid.*, p. 261.

CHAPTER XII.

NITROGENOUS MANURES.

THE most widely distributed nitrogenous manures are nitrate of soda (Chili saltpetre) and sulphate of ammonia. A third class of purely nitrogenous manures is that represented by animal waste. These latter products are of considerable agricultural importance, although those in the manure trade do not appear to recognize their value. These three forms of nitrogenized manures are not only differentiated by their chemical composition, but by their mode of action in the soil. They form therefore three distinct classes, which will now be examined.

Nitrate of Soda.—Nitric acid compounds have been known for a long period. It is probable, according to Herapath, that the ancient Egyptians used nitrate of silver to make their inscriptions on the bands in which they wrapped their dead; it is the same chemical compound as that known as infernal stone (lunar caustic) which is used to mark linen and the skin. So far back as the eighth century of the Christian era, Geber and Marcus described a body which they called *salpetræ*, which corresponds with saltpetre, nitrate of soda. In the twelfth century, Raymond Lulli called this body *salnitri*. Since then the term *saltpetre*, or nitre, has been used to designate nitrate of potash, whilst nitrate of soda is called Chili saltpetre, or nitre, in Great Britain.

Nitric Acid consists of nitrogen, oxygen, and hydrogen; its chemical formula is HNO_3. It thus contains fourteen parts of nitrogen (22·2 per cent), forty-eight parts of oxygen (76·19 per cent), and one part of hydrogen (1·59 per cent). It forms a very caustic fuming liquid (attacking organic matter, strongly burning the skin). In the concentrated state it has a density of 1·52 (104° Tw.), but the commercial acid is generally much weaker: D = 1·20 to 1·4 (40° to 80° Tw.). It decomposes easily, giving up a portion of its oxygen to oxidizable bodies, such as carbon, sulphur, sulphurous acid, and then passes to less highly oxidized states. Metallic zinc reduces dilute nitric acid, converting it into nitrate of ammonia. With bases it forms salts, which with the exception of some basic metallic salts, are soluble in water. Nitric acid is formed almost exclusively by the oxidation of ammonia, or of nitrogenous matter

of animal origin, under the action of the air in presence of bases (carbonate of lime). However, this spontaneous formation in the soil is very slow in our climate. It is, on the other hand, very rapid in Southern countries, Bengal, Hungary, Spain, S. America, where the conditions of temperature and of moisture in the air conduce considerably to the oxidation of nitrogenous animal matter.

For a long time these countries where nitrates exude spontaneously from the soil, and cover it with a layer like hoar frost, alone supplied Northern Europe, up to the time when they succeeded in making mixtures of soil to produce saltpetre. This industry was conducted in saltpetre fields. Limestone, marl, or washed wood ashes were mixed with animal matter, urine, dung, straw, etc. Heaps were made, which were left to themselves in the open air for nearly a year, frequently turning them. When the earth was ready, that is to say enriched, it was lixiviated. To eliminate the lime from the liquor obtained, it was treated with wood ashes, and clarified, and evaporated to obtain saltpetre. That method, which requires much work and only gives poor results, could only be applied in countries which, deprived from communication with the south, as in time of war, were obliged to live on their own resources, as France and Germany were during the continental wars. This method, therefore, was abandoned.

But the sources of saltpetre indicated above barely sufficed for the needs of industry, practically none of the material being available for agriculture. The discovery of an important deposit of nitrate of soda in America, the working of which was commenced in the years 1825-28, enabled this material to be used largely in agriculture.

Chili Nitrate of Soda.—South American nitrate of soda is distinguished, more especially from ordinary saltpetre, by the fact that its acid is combined with a different alkali. In Indian saltpetre it is combined with potash (KNO_3), whilst in Chili saltpetre it is combined with soda ($NaNO_3$). It is met with in the Pampas of Peru, of Chili, and Bolivia, between 19° and 27° of south latitude, abounding especially in the province of Tarapaca (formerly Peruvian, now Chilian) and in the desert of Atacama. The nitrous mineral caliche, or *terra salitrosa*, occurs as a layer 1 to 6 inches thick under a bed of conglomerate, consisting of sand, felspar, and pebbles, amalgamated by a cement consisting of clay and different salts forming a bed 20 to 30 inches thick. Its colour varies from grey to brown. The conglomerate bed is sometimes absent, in which case the mineral crops out at the surface.

The *caliche* is never pure nitrate of soda. It contains mixtures of nitrate of potash, common salt, iodide and bromide of sodium, alkaline sulphates and sulphite of lime mixed with sand. The proportion of nitrate on the average being only 25 per cent,

although picked pieces may contain more. The following gives the percentage of nitrate in different products :—

TABLE LXIV.—SHOWING COMPOSITION OF CALICHE.

	Saltpetre. Per cent.	Common Salt. Per cent.
Yellow salt, pure hard, with small crystals	77·9	12·9
Yellow salt, pure porous soft, with large crystals	65·7	28·12
Yellow caliche, veined with brown	64·73	32·02
White caliche, hard and with small crystals	60·50	14·30
White caliche, porous and large crystals	68·03	28·12
Brown caliche, porous and large crystals	36·80	20·70

Opinions differ as to the method of formation of this deposit, which occupies a surface of about 60,000 hectares (150,000 acres) and contains about 170,000,000 tons. Hillger's is the most likely theory; he believes that the nitrate is formed from the nitrogen of guano deposits, which covered the shores of a great soda lake by a process analogous to that to be seen in Hungary in our own time. The soda salts of the sea water would simply convert the nitric acid formed by the oxidation of its ammonia into nitrate of soda. This opinion has in its favour all the facts and circumstances met with in the deposit. Moreover, traces of guano are still found in the crude salts. To extract the crude salt a hole is dug in the ground 50 cm. (20 in.) in diameter; when the saltpetre bed is reached a chamber 90 to 100 cm. (35 to 40 in.) in diameter by 30 cm. (12 in.) deep, and 150 to 200 kg. (3 to 4 cwt.) of gunpowder is inserted. By exploding the powder by means of a fuse a considerable surface of the deposit is laid bare often on a radius 10 metres (40 ft.) from the hole. The crude salt is hand picked, to eliminate stones and fragments of less value; it is charged into baskets or into trucks, which camels transport or draw to the dissolving sheds. To dissolve the crude caliche three kinds of apparatus are used, viz. :—

1. *Open Cast-iron Pans—Paradas.*—These are heated by naked fires. Two pans 2 metres in diameter (6 ft. 6 in.) are used for one furnace. Well water or water from a previous operation is run in, then it is charged with caliche or crude saltpetre reduced to pieces the size of the fist. When the solution is concentrated enough, it is run into cases or boxes, where it clarifies; it is then decanted on the top of the depot and run into iron or wooden crystallizers; 40 per cent of crystals is thus obtained and 60 per cent of mother liquor.

2. *Cylindrical Vertical Pans—Maquinas.*—These are heated by direct injection of steam. They are 8 to 10 metres (26 to 33 ft.), with a diameter of 4 to 5 metres (13 to 16 ft.). Each of these pans yields in twenty-four hours 46 to 148 tons of saltpetre. The

clarified solution is poured into wrought-iron crystallizers 4 to 5 metres (13 to 16 ft.) square and 0·5 metre (20 in.) deep, crystallization lasting three to four days. The steam given off contains an important amount of iodine, which loss can be avoided by an addition of soda.

3. *Vessels heated by a closed tubular steam coil*, which have been introduced by the British and German companies. These vessels measure 11 metres (36 ft.), 1·85 metre (6 ft.) wide by 1·85 metre (6 ft.) high, into which the mother liquor and the wash water are run and heated to boiling, then six trucks of perforated wrought-iron containing about 4 tons of caliche. The nitrate dissolves in the water whilst the residue remains in the trucks. To hasten solution the liquid is agitated by the injection of steam and hot air under each truck by means of a Koerting's injector. This plant works more economically than the preceding. At the same time the solutions so obtained are purer and more concentrated. To produce a ton of nitrate 3 tons of caliche is required. The crystallized nitrate is left to drain, then it is dried in the open air. Nevertheless it always remains slightly moist owing to the presence of chlorides of calcium and magnesium, and possibly also of nitrates of calcium and magnesium. It crystallizes in rhombohedra, and has a dirty reddish-grey appearance, due to the presence of a small quantity of oxide of iron and bituminous substances. The residue left by the solution (*ripio*) still contains from 15 to 35 per cent of $NaNO_3$. It is boiled with water forming a weak solution of 43° to 45° B. which is utilized to dissolve a fresh charge of crude salt. The muds from the clarification are treated in the same way. According to Dr. Langbein, they contain 67·1 per cent of common salt and 27·3 of nitrate of soda.

A very full account of the Chilian nitrate industry has recently been given by I. B. Hobsbaum and J. L. Grigioin,[1] from which the following notes are taken. Caliche consists of a very variable mixture of insoluble matter cemented together with soluble salts. The analyses of caliches are given on opposite page.

In 1809 Taddeo Haenke, a German living in Bolivia, demonstrated the value of Chilian nitrate, and since that time the method of extraction has not varied except in details from the original, the object being to obtain a solution free from suspended matter containing as much nitrate of soda and as little sodium chloride and other salts as possible. This is done by working at a high temperature, sodium nitrate being very soluble in hot water, while in this concentrated solution sodium chloride is almost insoluble.

[1] "Jour. Soc. Chem. Indt.," 1917, p. 52.

	High Grade.				Low Grade.			
	1	2	3	4	1	2	3	4
Moisture . . .	1·107	2·003	1·121	2·764	1·061	1·892	2·173	1·951
Potassium nitrate .	—	—	—	—	0·958	—	—	—
Sodium nitrate . .	52·960	48·700	50·250	33·687	13·270	12·4	14·034	13·160
,, chloride .	23·4	17·3	30·2	25·7	29·3	13·9	17·8	9·1
,, iodate . .	0·074	0·151	0·026	0·014	0·059	0·062	0·010	0·152
,, sulphate .	2·976	6·958	1·226	—	8·220	9·075	—	6·246
Magnesium sulphate .	1·166	2·441	0·156	—	0·885	7·041	—	3·087
Calcium ,, .	2·585	2·177	3·110	3·230	4·026	3·618	5·456	3·346
,, nitrate . .	—	—	—	—	—	—	3·935	—
Insoluble . . .	15·677	20·213	3·9	34·597	42·213	51·934	56·543	[illegible]2·938
Total . . .	99·945	99·943	99·989	99·942	99·992	99·932	99·951	99·981

The above authors distinguish three historical periods: the first from 1809 to 1856 when the industry was unorganized and the operations of purification were somewhat primitive, the solution being performed in copper pans of native manufacture heated by open fires. During this period only the richest caliche was worked, containing probably as much as 80 per cent. of nitrate. During the second period, from 1856 to 1880, steam was introduced into the mixture of caliche and water. During this period the raw material was still very rich, it being stated on good authority that caliche containing less than 50 per cent of nitrate was not removed for treatment. In this period also closed steam coils were used for concentrating the liquors. In the third period, from 1880 to 1900, a very great improvement was introduced by Mr. J. T. Humberstone, consisting of the counter-current system which was adopted from the alkali works in England, known locally as the "Shanks system". In this system the untreated material is subjected to the action of a fairly concentrated solution obtained from a previous operation, while the almost exhausted material is treated with fresh water. These operations are carried out in a series of tanks, fresh water being pumped into the last of the series and then passing from one tank to another in which it comes into contact with less and less exhausted caliche until finally the strongest liquor is brought into contact with untreated material, from whence it passes to the crystallizing tanks. The tanks are heated by closed-steam coils so that as the liquor becomes more concentrated its temperature is also increased. The tanks are 32 × 9 × 8 ft. and are provided with false bottoms 9 to 12 in. from the true bottom. They are provided with three doors for discharging the refuse (*ripio*). The caliche is crushed with a

Blake's crusher to pieces varying in size from ¾ in. for hard material to 3 in. for the softest. The charge for each tank is 60 to 70 tons, and there are four or five tanks. The strong liquor (*caldo*) is run into settling tanks where the suspended matter separates either by settlement alone or after addition of flour or dung, etc., and the clear liquid is then run off into the crystallizing vats.

An average officina's working is given as follows:—

	Unit.		
Weight raw material	1000 tons		
Nitrate content 17 per cent	170 ,,		
,, produced (50 per cent yield)		85 tons	50 per cent.
,, in refuse			
Ripio at 3·4 per cent		34 ,,	20 ,,
Borra		17 ,,	10 ,,
Unaccounted losses		34 ,,	20 ,,
		170 ,,	100 ,,

Chilian nitrate of soda, ready for shipment, has the following composition:—

TABLE LXV.—ANALYSES OF CHILIAN NITRATE OF SODA.

	Per cent.	*Per cent.*
Nitrate of soda	94·0	15·48 N.
Common salt	1·52	
Potassium chloride	0·64	
Sodium sulphate	0·92	
,, iodide	0·29	
Magnesium chloride	0·93	
Water	1·36	
Boric acid	trace	
	99·60	

Better equipped factories supply nitrate of the following average composition:—

TABLE LXVI.—ANALYSIS OF BETTER QUALITY NITRATE OF SODA.

	Per cent.
Nitrate of soda	96·00
Common salt	1·00
Sulphate of soda	0·50
Insoluble	0·25
Water	2·25
	100·00

Common salt and soluble sulphates may be eliminated by washing with cold water and by centrifuging. The content in nitrate is evidently not always constant; it generally varies between 90 and

100 per cent, which corresponds to a strength in anhydrous nitric acid of 56 to 62·3 or of 14·8 to 16·4 per cent of nitrogen. In Great Britain the fraction which goes to make up 100 per cent is regarded as refraction, so that a nitrate of 5° of refraction means a nitrate of 95 per cent strength. This remark is important, as it serves to explain market reports. On different occasions chlorate and perchlorate of potash have been found in nitrates. Now these substances are liable to spontaneous combustion, besides they are injurious to vegetation. The presence of perchlorate is attributed to the negligence of the workmen who have omitted to cool the solution of caliche in the pan and have set it aside to crystallize in the hot state. This perchlorate may be extracted from the substance by the method which was the subject of German patent No. 125,206. But since the disastrous effect of perchlorate on vegetation has been recognized and the nitrates which contain it refused, manufacturers have been more careful, and perchlorate is now only rarely met with in nitrate.

One hundred parts of water dissolve of nitrate of soda at

0°	10°	20°	30°	40°	100	121°	boiling-point of the solution.
71	78	88	98	109	178	224·8	parts.

The specific gravity of nitrate of soda is 2·244.

Nitrate of Potash.—A compound of nitric acid with potash has no interest but for industry; it is too dear to be used in agriculture, for up to now it has been produced by leaching the soil around villages in India, etc., or is made from Chili saltpetre and potassium chloride. The potassium nitrate exported from India is obtained largely by leaching the earth around old village sites. The exports in 1912 amounted to 12,806, valued at £205,600, in 1913, 15,224, value £237,581, and in 1914, 14,157 tons, value £232,916. Deposits are also found in caves in India. After refining the product has a purity of 94 per cent.[1]

Chili saltpetre also contains a small quantity of potassium nitrate, and deposits of this salt have been discovered at Tacunga in Peru and at Cochabamba in Bolivia.[2] It forms in itself an excellent manure, seeing that it contains not only nitrogen, but also potash in a very pure form. Lately, however, important deposits of nitrate of potash have been discovered in South Africa, especially in the neighbourhood of Mabelstadt, and of Peliska in Cape Colony; these deposits do not, however, appear to have been exploited.

Before terminating this subject, mention may be made of a nitrogenous manure put on the market in 1874, which has given

[1] D. Hooper, "Agricultural Ledger," 1905, p. 17.

[2] T. S. Norton, U.S. Dept. of Commerce and Labour, Special Agents Series, No. 52.

good results. It is a double nitrate of potash and soda, containing in 100 parts, according to Maercker:—

TABLE LXVII.—ANALYSES OF A DOUBLE NITRATE OF POTASH AND SODA.

	I. Per cent.	II. Per cent.	III. Per cent.
Nitrate of potash	34·18	41·78	11·51
,, of soda	62·22	55·27	82·94
Common salt	2·67	0·57	3·43
Water	0·46	1·67	2·02
Therefore—			
Potash	15·90	19·44	5·35
Nitrogen	14·98	14·89	15·25

Storing and Handling of Nitrate.—Nitrate of soda is marketed in the original sacks (catch-weight) weighing 120 to 140 kg. (264 to 308 lb.). It forms a mixture of crystals of different sizes. It also absorbs moisture from the air and when it is preserved in sacks they rot after some time, and tear with the slightest strain. When the sacks are emptied, one part of the material, always moist, remains adherent to the fabric, from which there results not only a loss of material, but also a loss of sacks, since these gunny bags then become unutilizable and are liable to catch fire.

Nitrate of soda is often coloured yellow by the presence of chromate of potash or violet by the presence of nitrate of manganese, The presence of magnesium chloride renders it deliquescent; hence arises loss by the drainage away of liquid containing dissolved nitrate; that is why the bags are lodged on beds of plaster or clay which absorb the liquid. But it is best to spread the nitrate intended for mixing in not too warm a place. The bags are washed with tepid water, and the solution is added during the manufacture of superphosphate which has to be mixed with nitrate, or it is concentrated in a pan. Certain manufacturers content themselves with beating the bags free from the adherent salt. If the nitrate is to be employed alone it is screened and the lumps crushed in a Carr's disintegrator, or in the toothed roll crusher. It is dried in the old phosphate drier. However, if it be stored for a certain time in a place that is not heated, it gradually becomes moist. In consequence of the risk of fire, the building in which nitrate is stored should be isolated and built entirely of iron.

Production of Nitrate in 1907.—The exports authorized by the syndicate of nitrate of soda manufacturers of Chili, rose to 2,050,000 tons for the year 1 April, 1907, to 31 March, 1908. Of these quantities

1,750,000 tons had to be delivered before the end of the year 1907, and the remainder, say 300,000 tons, in the months of January, February, and March, 1908. Now these exports made from April to December, 1907, only amounted to 1,225,000 tons. The cause of this short delivery is due in the first instance to the labour crisis. The Chilian labourer, more fit than any other to work under the torrid sun of the Pampas, is as improvident as he can be. He only works when he must do so to live, and as wages are very high in nitrate factories he only works a few days, and then rests the remainder of the week; under such conditions the factories work very irregularly. The rise in the price of nitrate, which had been discounted by the syndicate of manufacturers, will always be limited by competition with sulphate of ammonia. The latter, in fact, after experiments made by Kraus at Weihenstephan, should produce the same effect as nitrate, with the difference that it acts more slowly.

Production and Exports of Sodium Nitrate.—The total production of sodium nitrate in Chili was:—

	1911.	1912.
Short tons	2,784,361	2,885,959

W. Montgemery & Co. in their annual reports give the following statistics:—

	1908.	1909.	1910.	1911.	1912.	1913.	1914.
Shipments to all parts for year ending December 31	2,017,000	2,100,900	2,300,000	2,412,000	2,478,000	2,660,000	2,0[illegible]0,000
Consumption in—							
United Kingdom	103,000	111,000	120,000	132,000	130,000	124,000	122,000
Continent	1,275,000	1,354,000	1,531,000	1,564,000	1,778,000	1,700,000	1,868,000
U.S.A.	309,000	407,000	501,000	556,000	481,000	608,000	553,000
Other countries	45,000	66,000	89,000	103,000	115,000	88,000	90,000
In the world	1,732,000	1,938,000	2,241,000	2,355,000	2,504,000	2,520,000	2,633,000

Ammoniacal Salts.—Ammonia is a compound of nitrogen and hydrogen, having the formula NH_3, and forms one of the decomposition products of nitrogenized organic matter. It is a gaseous body, having a characteristic pungent odour. It is very soluble in water, being the solution generally known as ammonia. It has an alkaline reaction, and turns red litmus paper blue. Under the influence of the oxygen of the air, with favourable conditions, ammonia is partially converted into nitric acid. It forms salts with acids, combining with them in the form of a metallic radical NH_4 which is ammonium. Thus sulphate of ammonia is formed according to the equation:—

$$H_2SO_4 + 2NH_3 = (NH_4)_2SO_4$$

and ammonium chloride according to the equation :—

$$HCl + NH_3 = NH_4Cl$$

All ammoniacal salts give off ammonia when they are placed in contact with alkalis or caustic lime. Ammoniacal compounds are very widely distributed in nature, but always in small quantities. Their presence has been determined in the air and in rain water, also in the juice of almost all plants. Ammonium chloride is found in salt springs, in volcanic emanations; carbonate of ammonia in large quantities in the guano deposits of Peru, Bolivia, and Chili, and the western part of Patagonia. The principal sources of ammonia for industry and for agriculture are certain substances of animal origin (bone, meat, blood) or vegetable (coal, peat), which, submitted to dry distillation, give off the greater part of their nitrogen as ammoniacal compounds.

Ammonia is, likewise, obtained by the distillation of fæcal matters in presence of caustic lime and by the treatment of gas (wash) liquor. Left to stand, urine putrefies; the urea is transformed into ammonia, which, treated by caustic lime, yields ammonia and carbonate of lime. Ammonia is also found in the smoke of factory chimneys and in coal soot; the latter may even sometimes be utilized as a manure, as the following analysis by Hutton of Glasgow of coal soot shows :—

	Per cent.
Potash	0·30
Phosphate of lime	3·20
Ammonia	2·80
Equal to nitrogen	2·30

Formerly, ammoniacal salts were made solely from matters of animal origin. They were charged into retorts which were heated to incandescence, the vapours given off being condensed. The carbonate of ammonia thus obtained was collected and purified or combined with acids to form different salts. The process is still applied in the manufacture of small quantities of sal-ammoniac, but solely as a by-product in the manufacture of animal charcoal. The calcination of the bones is done after two different methods. The one, the older, consists in charging the raw material into vessels placed in a furnace in stages so that one serves as a lid to the other underneath. The vapours given off during combustion, the details of which need not be dwelt upon, escape outwards by the chimney. The other method consists in calcining the bones in a cast-iron retort analogous to that used in distilling coal. The gases which are given off are collected and condensed. The products of the condensation contain among other useful substances ammonia, which

can be extracted by distillation and converted into sulphate of ammonia. But, as already observed, bone-black is no longer used in sugar factories. With the disappearance of bone-black, the by-products, especially ammonia, ceased to be produced. The most important source of ammonia is at present coal, the percentage of nitrogen in which varies from 0·5 to 1·6 per cent. The extraction of ammonia will therefore be studied in the following order: (1) In the manufacture of gas; (2) in the manufacture of coke; (3) in the blast furnaces, and (4) in the gas producers (Mond's process, Bourgeois and Lencauchez' process).

Manufacture of Sulphate of Ammonia by Distillation of Gas Liquor.—When coal is distilled, the nitrogen which it contains passes partly into the tar as complex products (aniline and its analogues) and partially in the form of ammonia in the illuminating gas. The ammonia is eliminated from the latter by washing with water. According to Roscoe, only 14·5 per cent of its nitrogen is obtained from coal as NH_3, 35·26 per cent is lost as free N, whilst the coke retains 48 to 68 per cent. This low yield of ammonia is due to the facility with which this gas is decomposed (at a temperature of 500° C., Ramsay and Young). This loss may be avoided by preventing the gas in the retort from coming in contact with the heated sides. According to Beilby, this desired result is obtained by distilling coal with steam. By this method as much as 50 to 56 kg., i.e. 110 to 123·2 lb. of sulphate of ammonia per ton of coal may be obtained. Gas liquor consists in reality of a weak solution of ammonia, carbonate of ammonia, sulphide of ammonia, cyanide of ammonia, and sulphate of ammonia. Its nitrogen content varies considerably, as the following analyses by Arnold, in 1889, show:—

TABLE LXVIII.—ANALYSES OF GAS LIQUOR FROM COALS OF DIFFERENT ORIGIN.

One litre of gas liquor contains the following ingredients in grammes, or 100 gallons contains in lb.	Gas Liquor from the Coal of				
	Zwickau.	Zwickau.	La Rhur.	La Saare.	La Saare.
Total ammonia	12·09	9·40	18·12	15·23	3·47
Hyposulphite of ammonia	1·036	1·628	5·032	2·072	6·296
Sulphide of ammonia	6·340	0·646	6·222	2·468	1·428
Bicarbonate of ammonia	1·050	1·470	2·450	33·763	5·856
Carbonate of ammonia	4·560	7·680	33·120		
Sulphate of ammonia	0·462	0·858	1·320	4·922	1·926
Ammonium chloride	30·495	17·120	3·745		

According to the same author, the ammoniacal liquor from a British gas works contained in grammes per litre (lb. per 100 gallons):—

TABLE LXIX.—ANALYSIS OF BRITISH GAS LIQUOR.

	lb. per 100 gallons.
Ammonia	20·45
Sulphur total	3·92
Ammonium sulphide	3·03
,, carbonate	39·16
,, chloride	14·23
,, sulphocyanide	1·80
,, sulphate	0·19
,, thiosulphate	2·80
,, ferrocyanide	0·41

It will be seen from these analyses that carbonate of ammonia preponderates; the percentage of ammonium chloride is likewise high.

Production of Ammonia in the Manufacture of Coke.—Although in the very beginning of illumination by coal gas steps were taken to collect the ammonia produced in the purifying of the gas for consumption, this was not so in the manufacture of coke, where this product was for a long time totally neglected. The coke industry, as it is now conducted, yields products identical with those from gas. The first attempts at recovery of the ammonia were made by Stauf in 1764 in a Saarbruck foundry. But it was not until 1858 that Charles Knab constructed at St. Denis the first plant that gave good results, introduced by Carvès at Commentry in 1762. It was erected in 1866 at the Besseges Forge, then in 1879 at *Terre Noire*. In 1882, Simon of Manchester improved the Carvès coke oven by recuperating the heat to preheat the air to 500° C. or 600° C. The shape of these ovens was completely altered. Knab's ovens, wide and flat, heated under the sole only, and carbonizing at a low temperature, have been completely abandoned to give place to Carvès, Simon-Carvès, Otto and Semet-Solvay ovens, high, narrow, long, carbonizing rapidly and at a high temperature. The furnaces actually in use may be divided into two classes:—

1. Those which are only a modification of the ordinary coke oven, where the heating is effected by the admission of air into the interior, thus burning a part of the carbon as fuel (Jameson, Aitken, Luhrmann types).

2. Those in which air is not admitted into the interior, the heat being applied to the exterior by the combustion of the gas which escapes during distillation, and after separation of tar and ammonia. Almost all modern coke ovens belong to this class (Hoffmann Otto, Simon-Carvès, Bauer, Hussener, Semet-Solvay, etc., types). Here, in a few words, is the general principle followed in coke ovens of the present day. All are built, apart from numerous details, in such

a manner as to have a hermetically sealed chamber, from which the gas distilled from the coal is aspirated mechanically without admission of air. The gas afterwards passes through condensers, cooled on the outside by air or water, where they deposit the greater part of the ammonia and the tar; the small remaining portions being deposited in the scrubbers (coke columns). The residual gas is then led to the *tuyeres* which heat the retorts, and inflamed by means of a current of hot air issuing from the recuperators. After having accomplished this heating, the hot gases pass into the heat recuperators. Certain German coals yield 11·5 kg. (25·3 lb. of sulphate of ammonia. By the Semet-Solvay ovens, as much as 7 to 17 kg. (15 to 37·4 lb.) of sulphate of ammonia per ton of coal distilled are obtained.

The working of these ovens is regulated by various conditions. The coal introduced into the oven ought, to give a good coke, to be instantaneously submitted to a very high temperature, and the calcination must be conducted rapidly and continuously. That is why the heat is transmitted through as thin walls as possible, as in the Semet-Solvay oven. In the Hoffmann Otto oven the gas given off by distillation escapes through two orifices in the arch of the oven and passes into gas reservoirs placed above and across the ovens; then it is lifted by aspirators, and drawn through pipes to condensers and washers, in which the tar and ammonia are deposited. Freed from these two substances the gas is brought back through another pipe, under the sole of the ovens. The inflamed gas follows alternatively vertical flues, ascending one half of the flues and descending the others. In the Semet-Solvay system the flues in which the gas burns, and which generally are fitted into the main flue, are here independent, and consist of retorts with their encased sides, the one in the other, forming a complete and tight circuit.[1]

The Carvès, the Tamaris, the Terre Noire, and Bessege ovens, producing together about 300 tons of coke per day, yield 6 tons of tar and 2 to 2·5 tons of sulphate of ammonia.

The advantages of recuperation become more and more evident, and in spite of the expense which the installation of such plant involves, many mine proprietors have not hesitated to build ovens of this type.

The working of a battery of four coke ovens entails a supplementary staff to work the gas-extractor, and to keep in order and clean the recuperation appliances. The cost of the Semet-Solvay furnace, refractory masonry with lining, oven discharger, discharger

[1] The Hoffmann Otto is 10 metres (40 feet) long, 0·4 to 0·6 metre (16 to 24 inches) wide, by 1·70 metres (5 ft. 8 inches) high. The Semet-Solvay is 9 metres (30 feet) in length, by 1·70 metres (5 feet 8 inches) high, and of a width, varying according to the quality of the coals to be treated, of 0·36 to 0·42 metre (14 to 17 inches). The air is heated to 200° to 300° C. (392° to 572° F.).

flue, water piping, etc., is £240. The extractor, pump, and recuperation appliances cost £140. Each oven produces 5 tons of coke; the operation lasting about twenty-four hours. The Hoffmann Otto takes a charge of 5 to 6 tons. The use of these ovens has extended very rapidly in France; there being at present several hundreds of them. The Hoffmann Otto are almost exclusively used in Germany and Austria. The Semet-Solvay are used in Belgium, France, Great Britain, Germany and the United States.

Direct Ammonia Recovery Process.—In connection with coke ovens the ammonia is now extracted by what is known as the direct recovery process. In this process the gases are passed direct into sulphuric acid in the saturater without preliminary treatment. This method, although working quite satisfactorily with coke oven gases has not been so successful when applied to gas works. Two methods of working have been devised known as the Otto and the Kopper's systems. In the Otto system the gas, which has a temperature of about 160° C., is subjected to the action of a liquor jet injector and a Pelouze extractor for removal of the tar and is then passed directly to the saturater. It is necessary, however, to impart additional heat to prevent dilution of the liquor in the saturater, otherwise the sulphate of ammonia does not crystallize. In the Kopper's system the tar is condensed by cooling and the condensed liquor which also separates is distilled with lime in a column still, the ammonia evolved being returned to the crude gas. The cooled gas is passed through the tar extractor and then through a heat interchanger in which it is heated by the hot crude gas to a temperature much above its dew point, e.g. 65° to 70° C., it is then passed into the saturater. The sulphate of ammonia produced by the Kopper's system is of a better colour than that obtained in the Otto method, besides which naphthalene stoppages are entirely obviated.[1]

Recovery of Ammonia from Blast Furnaces.—The recovery of the ammonia contained in the gas from blast furnaces is relatively modern. The coal used is a non-caking coal, which prevents previous conversion into coke. The gases escaping from the furnace mouth pass through a series of pipes into apparatus similar to those used in gas manufacture, followed by a series of scrubbers, fitted with perforated plates, leaving the gas to pass alternatively on each side, whilst a thin stream of water, constantly flowing, dissolves the ammonia. The liquid is repumped and sent back to the scrubbers, until sufficiently saturated. The yields are on an average 0·9 to 1·36 per cent of the weight of the coal, which corresponds very nearly with the amount of ammonia obtained from the Carvès coke ovens.

[1] A. Fürth, "J. Gasbeleuct," 1911, 1030. See also Reports of the Chief Inspector of Alkali Works, 1915, 1916, and 1917.

Recovery of Ammonia formed in Gas Producers.—Heating by the gas obtained in the semi-distillation of coal is one of the most economical processes now known. It obviates various drawbacks incidental to the use of a great number of fires, and enables very high temperatures to be obtained. In this distillation, as in all similar treatment of coal, there is given off at the same time as the combustible gases an appreciable amount of ammonia. To give good results the production of the gas is effected by an alternation of two following operations:—

1. The vapour of superheated steam is directed on to coal, heated to incandescence, which lowers the temperature, owing to the heat absorbed by the decomposition of the water.

2. The combustion is stimulated by a current of air to bring the temperature to its initial point.

The gas produced in this second phase very much resembles gas from a gas generator, called Siemens' gas. The mixture of air and steam is suitably adjusted. Amongst the gas generating plant constructed on this principle mention may be made of Siemens', Schilling's, Powson's, Wilson's and Mond's.

1. *Mond's Process.*—Mond was the first to inaugurate in England this new process of extracting ammonia from the products of combustion of coal itself. Coal is burnt in the gas generator in a mixture of air and steam, in such proportions that two tons of steam are used per ton of coal distilled. The temperature of the combustion is lowered to about 500° C. (932° F.). This excess of steam favours the production of ammonia; only one-third of the steam which passes through the generator is decomposed. The gas producers are rectangular in form and arranged in series. They are 1·82 metres in depth and 3·65 metres long. The ash pits are fitted with a hydraulic joint capable of resisting 0·10 metre water pressure. The air arrives above the level of the ash pit. The gas escapes from the centre at the top of the gas producer.

The gas which escapes from the gas producer traverses a washer with blades, Standard type, in which the ammoniacal salts are dissolved. Then at a temperature of 100° C. it passes into the first scrubber, which is drenched with a 38 per cent solution of sulphate of ammonia to which a known amount of sulphuric acid has been added.

The gas contains at its entrance into the scrubber 0·13 per cent of ammonia by volume, it now only contains 0·013 when it issues at a temperature of 80° C. It then enters the condenser containing wooden baffles pierced with holes, where it meets a current of water which is heated to 78° to 80° C. (172·4 to 176° F.) in condensing the steam. The gas, purified and cooled, passes to the burners. The hot water obtained passes to a third scrubber, into which a current of cold air is passed, which it saturates with

moisture, and which brings the temperature to 76° (168·8° F.). That air is then forced into the gas producer. The yield obtained has equalled 32 kg. (70·4 lb.) of sulphate of ammonia per ton of coal, which is an exceptionally good performance.

Attempts have been made to produce ammonium chloride direct by introducing hydrochloric acid gas into the furnace or by mixing the fuel with clay impregnated by calcium chloride. The results were, however, not satisfactory.

Hennin proposes to operate like Mond, but by using high-pressure steam slightly superheated and suitably diffused in the mass of the fuel, in the proportion of 0·75 to 1 ton of coal.

2. *Bourgeois and Lencauchez' Process.*—Bourgeois and Lencauchez have patented a process the object of which is to collect the tar and ammonia in the gas distilled from coal, this operation not diminishing the calorific intensity of the gas. The plant which they propose to use, therefore, appeals to all those engaged in industries in which heat is required, glass works, metallurgical industries, etc., where, instead of burning coal under ovens, it is converted into gas in any kind of gas producer. It consists of three main columns. The first, for cooling and washing the gases, is intended to retain tar and oils, which are collected in a lower cistern. In the second, the gas charged with ammonia meets a shower of acidulated water. The third is intended to extract the last traces of ammonia and to convey them into the first, and so on. From the preceding it will be seen that those industries which formerly did not utilize in any way the nitrogen contained in their fuel, are going to become one of the most important sources of ammonia.

Manufacturing Plant.—In the various ammonia-producing industries which have just occupied our attention, the extraction plant consists, more particularly, of condensers and distilling columns.

Condensers.—The condensers are generally refrigerators, the extractor, the washing condenser of some kind of system, and the scrubbers, or coke columns. Refrigerators are used in the manufacture of gas. The issuing gas is aspirated by the extractor, which is in essence a suction and pressure pump. There exist a number of washing condensers. The following are mentioned: The Standard washer, the Chevalet washer, the Lunge Plate washer, the Pelouze and Audoin washer. The Standard washer consists of a series of cast-iron compartments, variable in number and dimensions according to the capacity of the plant. Each compartment contains a certain number of wrought-iron discs bolted together and locked on the shaft. These discs of thin sheet-iron, 2 to 3 mm. ($\frac{1}{12}$ to $\frac{1}{8}$ inch) thus present an enormous absorption surface. The latter traverses the washer in an opposite direction to the gas;

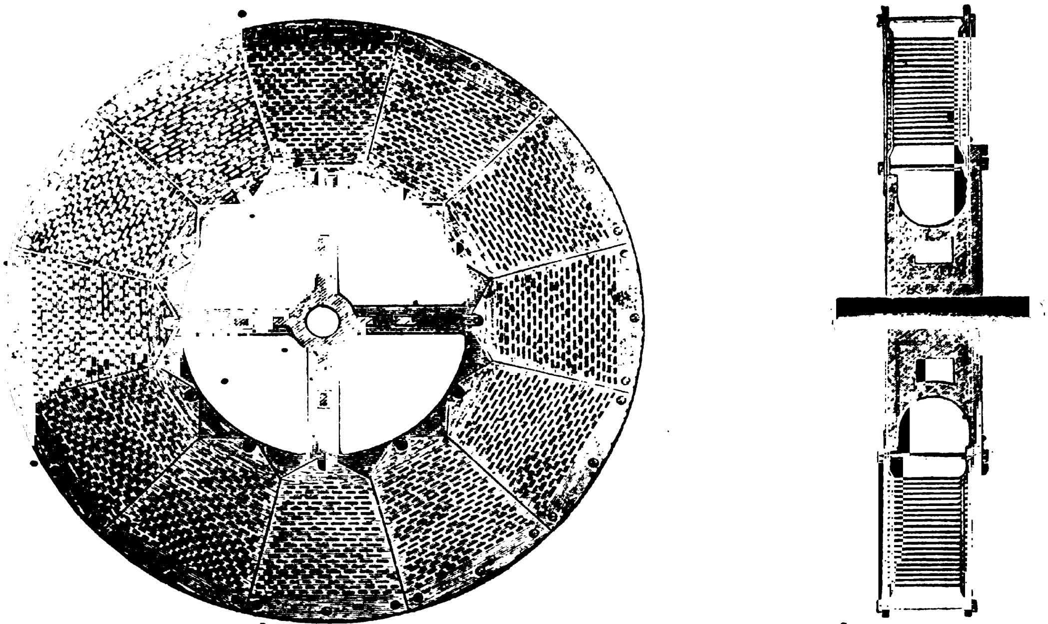


FIG. 38.—Plan and Section of Wooden Discs of the Standard Washer.—The disc is mounted on a central vertical shaft, from which radiate four bosses, supporting the part in the form of a crown, which is the essential organ of the apparatus. This crown is bounded above and below by wooden plates, in the intervening space of which there is arranged a multitude of small wooden prisms; the extremity of these is seen in the left-hand figure, and they are seen at full length in the right-hand section. They are rods which, dipped in the water at each turn of the disc, present a considerable absorption surface for the ammoniacal gas which comes in contact with them.

the discs half dip into the water. An improvement has been made by replacing the sheets of iron by pieces of wood, cut in the form of a prism and arranged in quincunxes. This apparatus is almost exclusively used in Great Britain. The washers restore to the scrubbers their true rôle, which is to arrest the last traces

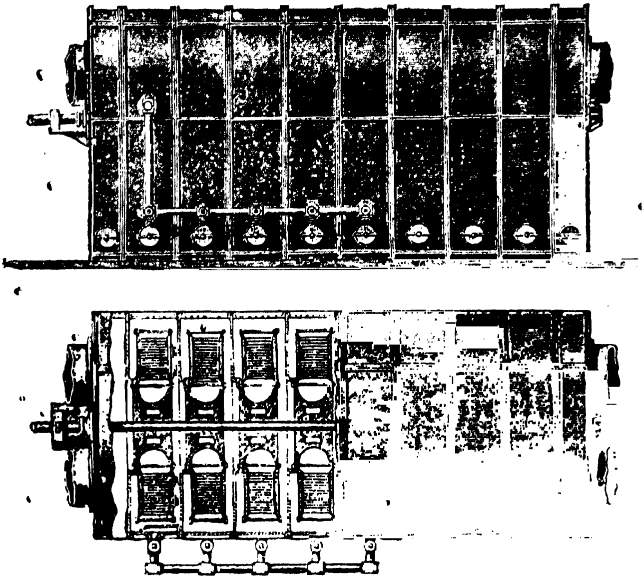


FIG. 39.—Standard Washer furnished with its different Discs.—The upper figure shows the outside appearance of the face of the washer; in the lower figure the washer is seen from above; the casing having been partly removed to show the interior arrangement. The discs of Fig. 38 are shown mounted side by side on the same shaft; their lower part dips in the water when the shaft revolves; the moistened discs come in contact with the gas which passes to the upper part. A peculiar system of partitions forces the gas to enter into intimate contact with the rods of the discs and ensures complete solution.

of ammonia. The packing of the scrubbers is composed of various materials; sometimes washed coke is used, sometimes wood shavings, fragments of pumice stones, or of perforated bricks. The packing should be done carefully, for on it greatly depends the amount of water to be introduced. A driblet of water, completely spread over well-arranged materials, will give as good an

absorption as enormous quantities of water pouring over loose materials. The water escaping from the scrubbers should be carefully controlled. The density of the ammoniacal water ought to be taken, and it must be ensured that the escaping gas contains no trace of ammonia.

Chevalet constructed a scrubber of wrought-iron or of cast-iron, containing cast-iron vessels 8 inches apart and pierced with a great number of holes, carrying a chimney a little less in height than the edge of the vessel. Each vessel is fixed in a ring without bottom of the distilling column. Between each vessel wooden shavings or coke is packed.

Distilling Plant.—The methods used in the manufacture of sulphate of ammonia consist essentially in disengaging ammonia from its salts, submitting it to distillation, conducting the ammoniacal vapours into a receiver containing sulphuric acid, and if necessary evaporating the solution obtained, so as to extract from it the sulphate of ammonia by crystallization. The ammoniacal salts are decomposed by lime, which is added to the gas liquor before distillation. In the older distilling plant heated by open fires the use of lime required precautions, because it was liable to adhere to the bottom of the boilers; in modern plant heated by steam this drawback has disappeared. Sometimes two methods are combined, that is to say, the gas liquor is first distilled alone and then it is redistilled after adding lime. The latter is used either as quick-lime or as milk of lime, and in quantity varying with the content of the ammoniacal liquor. But the amount used never exceeds 5 per cent of the material. The distillate consists mostly of a mixture of water and free ammonia; organic bases—the most volatile—are also present along with tarry matter. As amongst all these bodies ammonia is the most volatile, the principle of hot or partial condensation has been applied to its distillation, a method which is especially important in the distillation of alcoholic liquids. In the older plant the distillate traversed one or more vessels containing preheated ammoniacal liquor. By this arrangement the ammonia was separated from the less volatile products which condensed in the liquid; on the other hand, the ammoniacal liquor was brought to a high temperature before being distilled. However, this method cannot be adopted except by working continuously. The plant used in distilling ammonia may be divided into two classes, viz. (1) *open fire stills* and (2) *steam stills*. Although less economical and of much smaller output, open fire stills have still numerous advocates, because their installation is generally less costly and their management very simple. A few stills of both types will now be described.

Open Fire Stills—The English Still.—An old fashioned still which is to be found in use in certain English factories where it

gives excellent results is that shown in Fig. 40. It consists of a small boiler A, which is fed with gas liquor from a reservoir. If the liquor be heated to boiling, the free ammonia, the carbonate, the sulphide, and the cyanide of ammonia, all very volatile products, are given off with the steam, rise in the pipe *a*, pass into pipe *g*, whence they pass by the pipe *c* into the lead-lined wooden vat C containing concentrated sulphuric acid. The latter absorbs the gas and the vapours with effervescence, which renders them liable to return into the chamber A. To avoid this mishap a valve *h* is fitted to the upper end of the pipe *c*, which opens inwards, only allowing air to enter as soon as the acid begins to rise in *c*, i.e. as soon as the pressure in the apparatus is lower than the atmospheric pressure. When the operation is thought to be sufficiently far advanced, the test tap *d* is opened and the vapours coming from the

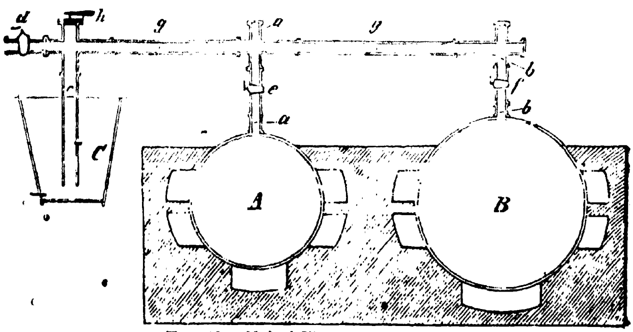


FIG. 40.—Naked Fire Ammonia Still.

boiler are tested with red litmus paper to see if they still contain an important proportion of ammonia. If the test shows that the liquor is exhausted it is run into the boiler B, placed at a slightly lower level alongside the boiler A. With this end in view the boiler A communicates on the opposite side with the boiler B by a pipe D (Fig. 41), which is naturally at a level high enough not to be reached by the fire. It suffices to open the taps *e*, *f*, *i*, and *k*. Milk of lime is added in the boiler B to the water from A. The boiler A is recharged, and the taps *i* and *k* being closed, the contents of the two boilers are brought to the boil, whilst the same process goes on as already described in the boiler A; pure ammonia gas is formed in the boiler B as the result of the decomposition by the caustic lime of the chloride and sulphate of ammonia still contained in the water which had been heated in A. This gas also passes into the vat C; when a test at the test-tap shows that all

the ammonia is volatilized, it is presumed that all ammonia has been expelled from the liquid in B, the latter is then run off. For that purpose the pipe D is fitted with two short pieces *m* and *l* closed with wooden plugs. To run off the liquid all that has to be done is to open them as well as the tap *k*. Ammonia can also be distilled in a single boiler, taking care to mix the milk of lime with the gas liquor beforehand. As the residual liquid would then contain not only chloride and sulphate of lime, but also carbonate of lime and various other salts, and as the mass of these insoluble salts would greatly hinder distillation, it is better to use two boilers, besides the bottom and sides of the boilers would become encrusted with a scale which, being non-conducting, would interfere with the proper heating of the vessels. When the sulphuric acid in the vat C is saturated with ammonia it forms a fairly concentrated solution of sulphate of ammonia. In the first phases of the operation this acid is greatly diluted by the steam mixed with the vapour of ammonia, but as the acid becomes heated considerably, the steam subsequently passes through without being condensed.

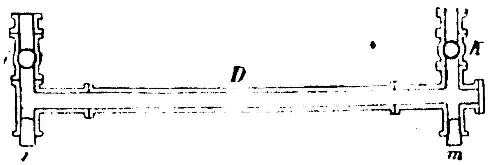


FIG. 41.—Details of Pipe communicating with the two Stills of Fig. 40.

The solution of sulphate of ammonia is not, however, sufficiently concentrated to crystallize on cooling, but requires to be subsequently evaporated in flat becks of lead, iron, or wood heated by a closed coil. This operation must be done with care. Under the influence of heat the organic matter contained in the solution exercises a reducing action on the sulphate of ammonia; ammonium sulphite, hyposulphite and sulphide of ammonium are formed, substances which strongly attack the metal of the apparatus; as, moreover, this reduction gives rise to a great loss of ammonia in the form of ammonium sulphide which is very volatile, the heat should be moderated as soon as the smell of this latter product is perceived. Evolution of $(NH_4)_2S$ or H_2S is an infringement of the alkali act. When the solution is sufficiently concentrated it is run into iron tanks, in which the ammonium sulphate is deposited as it cools. The mother liquor which flows from the crystals still contains a considerable proportion of ammonia. Sulphuric acid is added to it and it is again used in vessel C; finally, it can also be evaporated and recrystallized. The mother liquor from this second evapora-

tion contains too many impurities again to yield sulphate of ammonia by crystallization. However, it still contains a notable proportion of ammonia, therefore it is finally run into the boiler B to extract the ammonia by distillation after adding milk of lime.

Mallet's Still.—This still is shown in Figs. 42 (front view) and 43 (longitudinal section of one of the batteries). It consists of two batteries of stills AA, BB, CC, DD, which work in parallel and im-

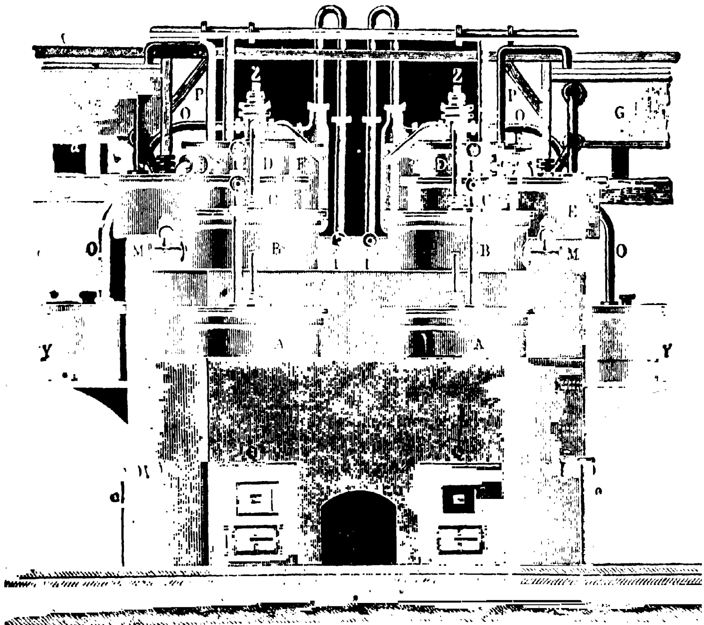


FIG. 42.—Mallet's Ammonia Still (front view).

part to it, as will be seen further on, great capacity of production. The stills A and B are fitted with perforated double bottoms in which the ammoniacal liquor, to which milk of lime has been added, is brought to the boil. They are fitted with agitators to keep the liquor in motion, to prevent any solids from adhering to the bottom. The ammoniacal vapours given off from these stills pass into the stills C and D, likewise filled with ammoniacal liquor, where they are washed to deprive them of compounds less volatile than ammonia. From the still D they pass into a coil 25 m.

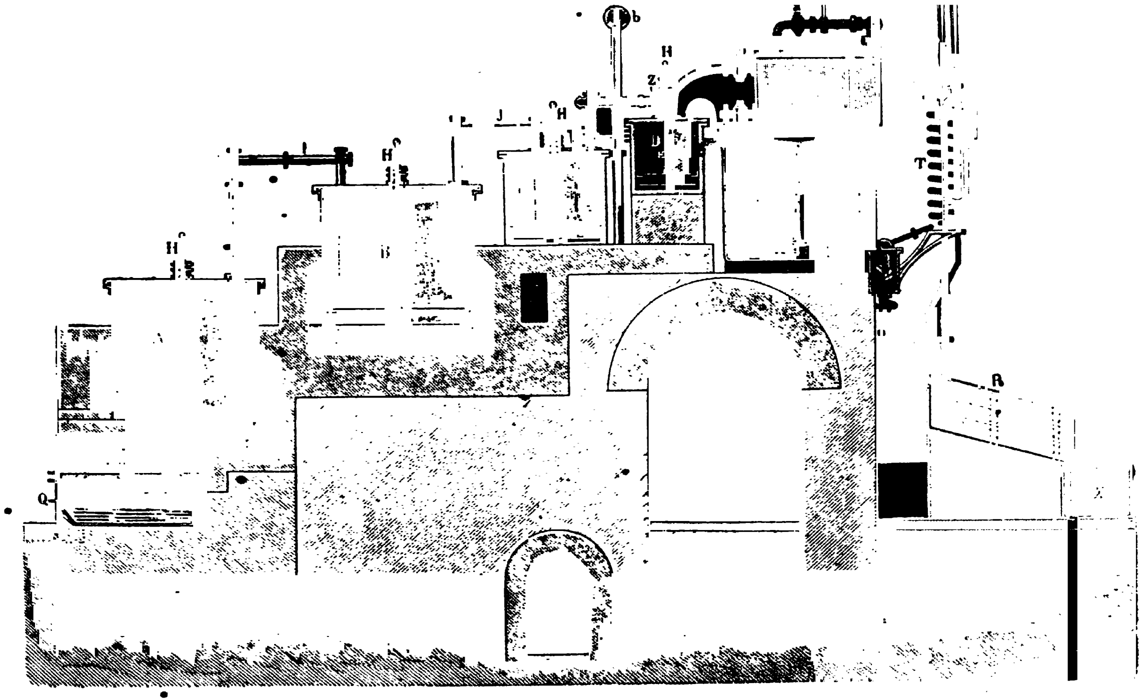


FIG. 43.—Mallet's Ammonia Still (side view).

(82 ft.) long, the spirals of which are contained in the receiver F, where they are cooled by ammoniacal liquor. The condensed ammonia flows into the vessel S, and from there into the collecting reservoir Y. The uncondensed vapours pass through a pipe, traversing the lid of the vessel S into an air refrigerator T. From there into the pipes U, fitted with a safety arrangement, which sends them into an absorption vessel placed behind R. The unabsorbed bad-smelling gases are absorbed by special arrangement. We have followed the progress of the ammonia driven off from the liquid under the influence of heat; let us now follow the reverse movement, i.e. that of the ammoniacal liquor used to feed the stills. This ammoniacal liquor is contained in a reservoir on a higher level, whence it passes into the measuring vessels G, through tap a; from that apparatus it first passes into the condenser F, where the steam brought by the coil gives up its heat to it and warms it; the ammoniacal vapours given off rise into G by the pipe P. The stills A, B, C, and D are fed by communication pipes not shown in the illustrations. As already stated, the ammoniacal vapours formed in the pans A and B pass into C and D, then into the condenser. The milk of lime is prepared in the reservoir E, whence it passes into the still B by the pipe M. The still A is emptied from time to time, say every three days; the discharged liquid is then replaced by an equal quantity of ammoniacal liquor coming from the stills B, C, and D. The condensed water in the vessel Y may be emptied into the vessel D through the pipe O. For that purpose the three-way tap Z, which brings two of the pipes entering D into communication, is fixed in the right place for the ammoniacal vapours not to pass into the refrigerator F, but into the reservoir Y.

The absorption vessel is lead lined and filled with the sulphuric acid intended to make sulphate of ammonia. The latter is put to drain in R, the mother liquor flows into X, and thence into the absorption vessel.

The air refrigerator T is only used when it is desired to make liquor ammonia. In the manufacture of sulphate of ammonia it is replaced by a cylinder 10 ft. high and 20 in. diameter, into which the pipe bringing the ammoniacal vapours dips, almost to the bottom. By fitting the cylinder with an overflow pipe, matters are so arranged that it is always one-third full. The water from the overflow pipe flows into the collecting vessel Y. The furnaces are shown at Q. The combustion gases first impinge on the still A, and then pass under the still B. The Mallet stills at work at the Vilette Gas Works produce 10 tons of sulphate of ammonia daily.

Lunge's Still.—This still is based on the same principle as the preceding, but it is much more simple; a is the *still*, b is the pipe leading the vapours to the condenser c. The refrigerator d is fed

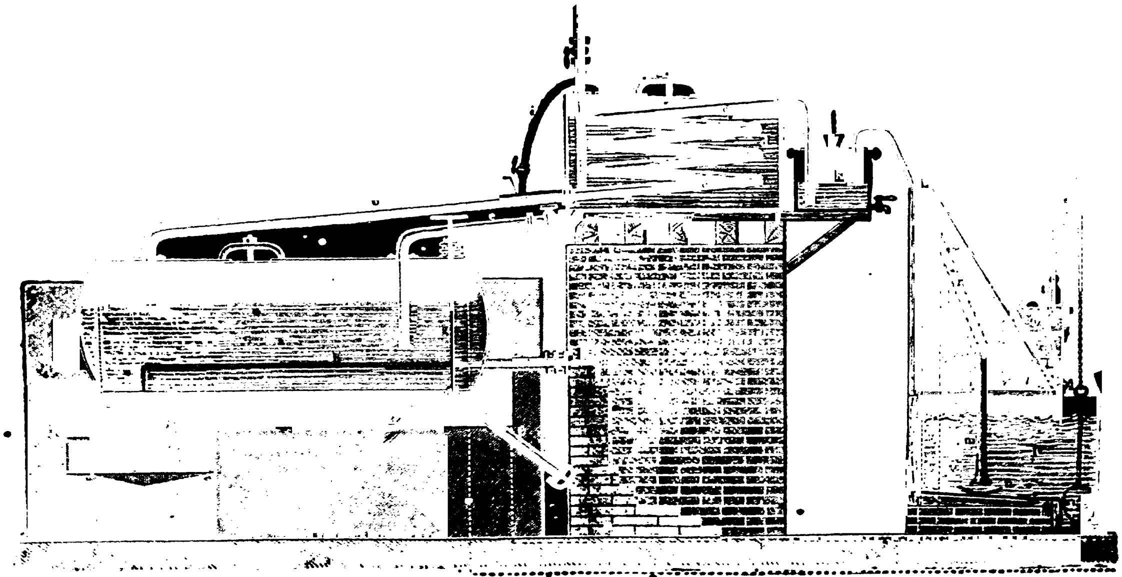


FIG. 44.—Lunge's Ammonia Still.

by ammoniacal liquor; it communicates with the still by the pipe *e*. The contents of the still may be run out by the pipe *f*, which is closed when the still is at work by a valve *g*. The lime which is deposited at the bottom of the boiler is again brought into suspension by the agitator *h*. The cock on the pipe *i* is opened when the liquid from the refrigerator *d* is heated to the point of giving off ammoniacal vapours; the latter pass through *i* into the pipe *b*, and afterwards into the coil *c*, mixing with the vapours coming from the still *a*. When the vapours have traversed the washer *k* they

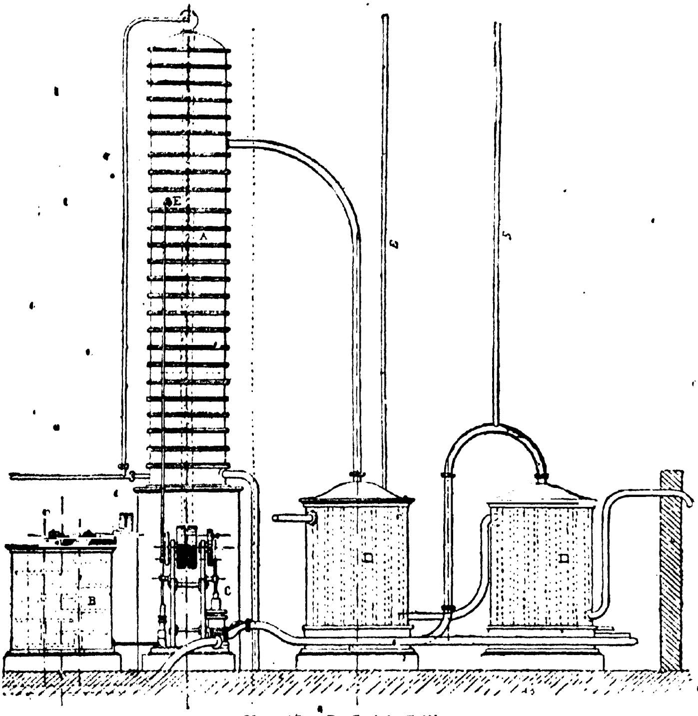


FIG. 45.—De Lair's Still.

A, Distilling column composed of circular segments of cast-iron. B, Milk of lime mixer. C, Milk of lime pump. D, D, Exchange heaters. Entrance of milk of lime into column. E, Gas escapement.

pass by the pipe *m* fitted with a safety arrangement into the lead-lined wood absorption vessel *l*, containing sulphuric acid to absorb the ammonia. The acid flows from the reservoir *o* through the syphon *p* into the absorption vessel *l*. Its arrival is regulated so that the liquid in the absorption vessel is always acid. The vapours given off collect under the hood *r*, whence they are forced into the

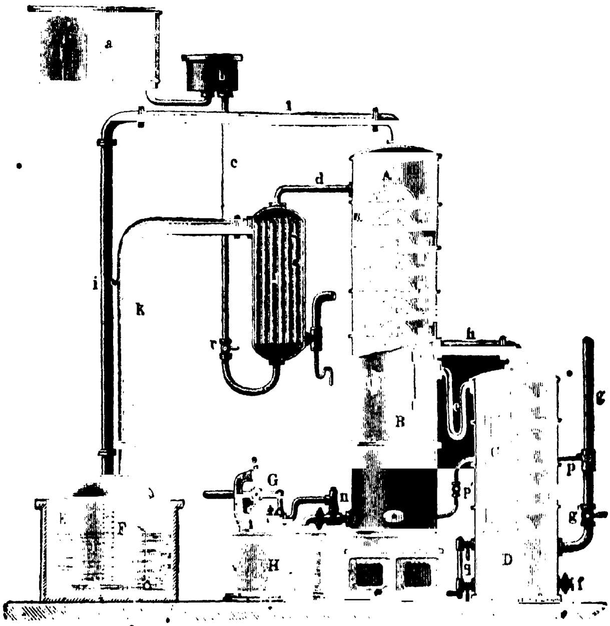


FIG. 46.—Feldmann's Ammonia Still.

chimney or burned in the furnace. The sulphate of ammonia deposited at the bottom of the vessel *l* is emptied by a bucket hung to a chain and counterpoise *t*.

Steam Stills.—The *intermittent*, naked fire stills have been replaced by *continuous* stills fitted with rectification columns similar to those used in alcohol distilleries. Such a column, the working of which is uniform and continuous, renders it possible to work much more economically. Amongst the best-known stills

of this nature, those of De Lair, Feldmann, and Gruneberg may be quoted.

Feldmann's Still.—The ammoniacal liquor contained in a reservoir *a* flows into a measurer *b*, passes through the pipe *c* fitted with a valve *r* into a tubular preheater J, rises through *d* into the rectifier A, where it meets the ascending steam which deprives it of all volatile ammoniacal compounds. Finally it flows into the lower part of the column or decomposition vessel B, into which milk of lime contained in the vessel H is forced from time to time by means of the pump G and the pipe *n*. The ammoniacal compounds which have resisted the action of steam alone are decomposed in B, where the liquid is kept in motion by a jet of steam injected through the pipe *p*. The ammoniacal liquor treated by the milk of lime, the non-volatile compounds of which are thus entirely decomposed, flows out in a continuous manner through the pipe *e* into a small column C, where the remaining ammonia is volatilized. The water, completely exhausted, collects in D fitted with a water level *q*, and runs out in a continuous fashion into *f*. The steam enters the apparatus by the pipe *g*, fitted with a valve *g'*; it passes through the column C, the pipe *h* and the column A, the pipe *i*, and finally, charged with ammonia, it enters the saturation vessel F, filled with sulphuric acid and cooled by the water of the reservoir E. The gases not absorbed in F, viz. steam, CO_2, H_2S, are led by the pipe *k* into the tubular preheater J, where they transfer their heat to the ammoniacal liquor. The sulphuric acid contained in the vessel F is sufficiently concentrated to allow the sulphate of ammonia formed to precipitate completely as soon as saturation is complete. The disengagement of heat accompanying the combination of ammonia with sulphuric acid gives rise to very energetic evaporation, which considerably facilitates the precipitation of the sulphate. Feldmann's stills work very economically and are used to a large extent in Germany. A large-sized still of this type will distil 44,000 gallons of ammoniacal liquor in twenty-four hours.

Gruneberg and Blum's Still.—In this still the liquor first passes into a tubular preheater B through the pipe *a*; it then ascends into the column A by the pipe *b*, and descends the column from plate to plate, meeting in its passage a current of steam; then it passes through the pipe *e* into the boiler F, which contains milk of lime, where the combined ammonia is liberated. The liquid gradually fills the boiler F, rises above the level of the pipe *f*, flows into the mud pocket *g*, passes out at *h*, spreads over the gradations of the column *i*, and runs away by the pipe *k* and the orifice *t*.

In the boiler G the water which now contains only a portion of the ammonia liberated by the lime comes in intimate contact with the steam, which is injected through the perforated coil *d*. The

steam forced by the concentric sides of *l* to rise along the gradations of the column becomes charged with the ammonia it meets, and passes by the pipe *m* into the pipes *n*, which force it to traverse the liquid of the milk of lime chamber. The ammoniacal vapours afterwards rise into the rectifier, and finally when they are entirely deprived of water they pass through the pipe *p* into the saturation vessel D. The evil-smelling non-condensable gases are collected in the bell *q*, whence they return through *r* and *s* into the preheater;

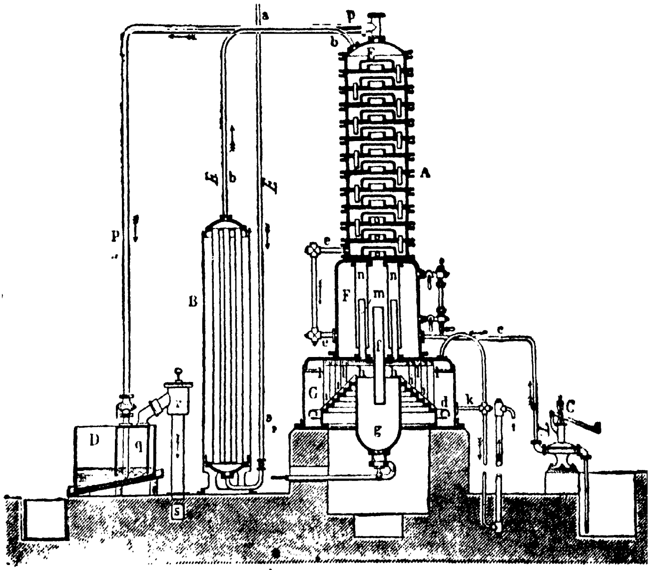


FIG. 47.—Gruneberg and Blum's Ammonia Still.

finally they are burnt in a special furnace. The milk of lime is injected by the pump C into the still through the pipe *c*. Stills of this type have been installed capable of treating 5500 to 7000 gallons of ammoniacal liquor in twenty-four hours. They work economically and require little superintendence.

Remarks.—Continuous stills should be entirely of cast-iron. Copper and bronze should not be used, since they are rapidly corroded by the ammoniacal vapours. The presence of ammonium sulphide in the ammoniacal liquor is very deleterious and in large quantity even poisonous. This body gradually corrodes even cast-iron vessels.

Therefore, iron reservoirs are sometimes replaced by cement ones. According to Kunheim, gas liquor may be freed from sulphur by a strong current of air, the effect of which is to decompose the ammonium sulphide into H_2S and NH_3.

Manufacture of Sulphate of Ammonia from Urine.—Amongst organic matters putrid urine is one of the most important sources of ammonia. The putrefaction of urine gives rise to the formation of carbonate of ammonia, urea CON_2H_4 decomposing as follows:—

$$CON_2H_4 + 2H_2O = (NH_4)_2CO_3$$

An adult produces on an average 30 grms. of urea daily which corresponds to an annual production of 24 kg. or 52¾ lb., nearly ½ cwt., of sulphate of ammonia. To gauge what this means, London with a population of, say, 5,000,000 produces in this way nitrogen equivalent

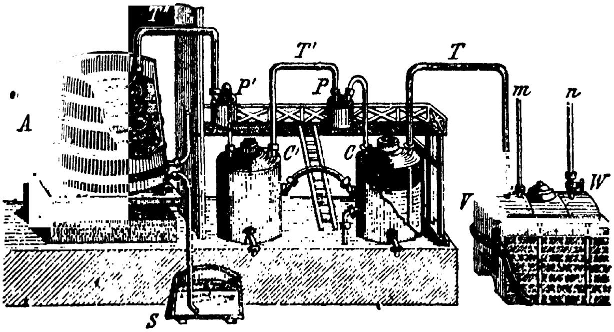


FIG. 48.—Figuera's Plant for Extraction of Ammonia from Urine.

to nearly 120,000 tons of sulphate of ammonia, worth at the present time (1919) £17 per ton, or a total value of £2,000,000 annually—the real loss is the value of the ammonia, which is £1,500,000—run into the sewers and finally out to sea.

As the carbonate of ammonia is very easily decomposed into CO_2 and NH_3, it has been thought advisable to utilize urine in the manufacture of sulphate of ammonia. Figuera used the following apparatus for the purpose. In the furnace V is the boiler W, which propels steam into the wrought-iron cylinders C C′ containing about 100 hectolitres (2200 gallons) by the pipes T and T′. The two cylinders are charged with putrid urine. The ammonium carbonate vaporized passes by T″ into the lead coil *c* in vat A; it condenses with the water and passes in the state of solution into the vessel S filled with sulphuric acid, where it is converted into sulphate of ammonia. The liquid used to cool the coil in the vat A, containing

about 250 litres (55 gallons), is putrid urine, which thence passes into the cylinders C and C′ by a pipe not shown in the figure. The boiler W contains the hot liquor not entirely exhausted from a previous distillation which still contains a small proportion of NH_3. The pipe T leads the steam into the vessel C: *m* is a pipe which dips a little above the bottom of the boiler whilst its other end passes outside the factory roof: *n* is a safety pipe which indicates at the same time (by the ascent of balls of froth) if the level of the liquid has lowered to the end of the tube *m*; *o* is a discharge pipe. The vessels P and P′ are to retain the abundant froth which would otherwise contaminate the distillate. To ascertain the level of the froth in the vessels P P′, these are fitted at different heights with three lateral apertures closed by wooden plugs, through which the froth flows when the plugs are removed: when the distillation, which lasts about twelve hours, is finished the boiler W is emptied and again filled with the urine contained in C C′.

Utilization of Peat in the Manufacture of Ammoniacal Salts.—For some years greater and greater efforts have been made to utilize peat in the manufacture of sulphate of ammonia. The abundance of the raw material, its cheapness and the facility of its extraction, and finally the unlimited outlet for commercial nitrogen as manure, are all factors which are in favour of the use of peat.

Numerous processes have been invented for the extraction of nitrogen from peat. (1) In that of Van Heeften (1905) the pulverized substance washed with HCl, then with ordinary water until neutral, is placed in the receivers arranged in diffusion battery style, where they are methodically exhausted by water charged with ammonia, which facilitates the solution of nitrogenous matters. The gas is extracted from the final product for re-use. But only nitrogen in humic acid combination is obtained, which restricts its use in the manufacture of chemical manures, and the value of which does not exceed that of organic nitrogen (*vide infra*). The value of the organic nitrogen of manures is increased by converting it into ammoniacal compounds. Rickmann (German patent, No. 8238) submits peat previously heated to from 350° C. to 800° C. to the action of a mixture of air and steam; but, as already mentioned, a great part of the ammonia is destroyed at such high temperatures, so that the yield is very poor. Waltereck (French patent, 345,399) obtains better results by heating peat either alone or mixed with other carbonaceous matters to a maximum temperature of 300° to 500° C., at which the mass is not incandescent. The mixture of air and steam heated to 300° C. (572° F.) is brought in contact with the peat in vertical iron retorts surrounded by refractory bricks. The temperature of the mass rises naturally up to 400° C. (752° F.); at which point the heating of the arriving gas is stopped, the heat produced by the reaction being more than sufficient to maintain the

emperature at a suitable degree. The arrival of the air is so timed as to oxidize completely the carbon of the charge in three to six hours. The quantity of steam should be proportional to the temperature. The inventor (cert. of addition No. 6407) has been enabled to suppress all fuel by replacing the steam with very finely pulverized water in the current of air injected. The ammonia is extracted from the gases by cooling with or without a spray of water; ammoniacal liquors are thus obtained which are treated as usual. As Muntz and Laine have determined, yields much superior to those by dry distillation have been obtained where the coke retains 1 per cent of nitrogen; a peat containing 2 per cent of nitrogen yields 1·6 to 1·8 per cent in the form of ammoniacal liquor.

Muntz and Girard distil peat (previously dried and crushed[1]) in a current of superheated steam. Water gas, mixed with ammoniacal vapours, tars, pyroligneous products, are produced. The combustible gas is used to heat the retorts; the distillation products treated with bicarbonate of soda residue from the extraction of the ammoniacal liquors yield NH_3 and CO_2, the latter re-entering into the manufacture; and acetates of lime and soda, methylic alcohol, and analogous products, accumulate in the mother liquors of the bicarbonate of soda, from which they are extracted by distilling the mixture of alcohols, and NH_3 neutralizing NH_3, and then redistilling. Finally, the residue from the distilled peat may be used as a substitute for animal charcoal in the manufacture of clarifying and purifying filters. The ammonia is present in the ammoniacal liquors principally as carbonate.

Gaillot and Brisset convert the organic nitrogen of peat into ammonia by slow combustion. The dry or moist peat—pure or mixed with other nitrogenous matter—is crushed, then fed into the hopper A of the oven (Fig. 49). The bottom of the hopper consists of a grating of flat bars capable of being rotated after the style of the laths of a metallic venetian blind, in such a way that if it be turned on its axis the charge passes entirely into the oven, which is at once closed. The combustion of the peat is fractionated into two stages; at first it passes from the top of the furnace into the distilling zone, where it is dried and then heated to convert it into a sort of coke. The gases produced charged with steam, ammonia, and tar pass into *h*. The barred grate C enables the admission of the incandescent coke into the zone of combustion to be regulated—a real furnace, where the peat burns before passing to the ash-pit.

[1] The drying of peat is a costly item even when air-dried. But here in wet seasons in many peat districts it cannot be air-dried: resource must therefore be had to artificial drying, and the whole manipulations—making and maintaining road to moss, casting, spreading, turning, cocking, carting, stacking, and crushing the peats—bring peat too near the price of coal for its treatment to prove remunerative.—Tr.

The ammoniacal gases, dry and very hot, pass out by the pipe utilized as a heating surface for the concentration of the ammoniacal liquors. Dampers F as well as shaking grates C and E enable the progress of the combustion to be regulated.

Recuperation of the Ammonia.—For the manufacture of fertilizers it is advantageous to substitute for simple condensation a

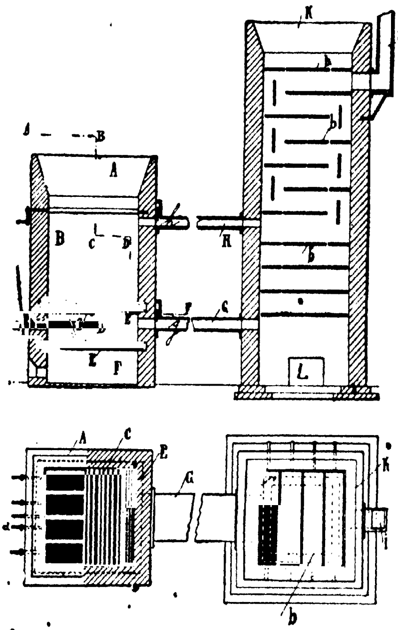


FIG. 49.—Gaillot and Brisset's Oven for Recovering Ammonia from Peat.

method of fixing the ammonia in a form immediately utilizable as a manure. The porosity of peat gives it a considerable absorptive capacity. Bacqua and Lorette use it to absorb the ammonia from the distillation gases. These pass into chambers containing perforated boxes arranged as baffles and filled with a mixture of peat, sawdust, and sulphuric acid, and are there deprived of all their ammonia.

Gaillot and Brisset use pure peat impregnated with acid solutions.

or mixed with superphosphate of lime as an absorbent. Their recuperator (Fig. 49) consists of a tower K, divided into ten stages by wide oscillating flat bars driven independently, so as to be able to regulate from the outside the forced methodical circulation of the absorbent of whatever nature it may be. The arrivals respectively of the hot and cold gas produced in their ovens, already described, are in G and H at heights calculated so that the space HI is sufficient for the gases escaping by the chimney I not to contain more than traces of ammonia, and that the path GH suffices to dry perfectly the manure reaching the discharge door of the oven L.

Muntz and Girard collect ammonia by condensation and bubbling, purify the ammoniacal liquors by distillation, then treat them with NaCl. Ammonium chloride and insoluble bicarbonate of soda are obtained; the carbonation is finished by a current of carbonic acid from the residual bicarbonate, then it is filtered. The calcination of the product enables the ammonia to be recovered, and gives CO_2 utilized for the next carbonation. The filtered solution contains an excess of NaCl and ammonia, as ammonium chloride and carbonate. The carbonate is separated by distillation, and calcined at a higher temperature. NaCl, equally soluble in the hot state as in the cold, crystallizes; it is separated, and there is finally obtained a very concentrated solution of ammonium chloride, which is crystallized. The product may afterwards be refined or used directly as manure.

Manufacture of Sulphate of Ammonia from Peat by the Mond Process.—After numerous unfruitful experiments on the utilization of peat, Dr. Caro has applied the Mond process, by which poor coals are utilized, not only to produce gas to drive motors, but also to utilize their nitrogen as sulphate of ammonia by giving to the gas producers an appropriate arrangement. Experiments made in this direction at Stockton by Mond for the utilization of peat have given very satisfactory results, and as a sequel to these an experimental factory was installed in Germany capable of treating 50 to 60 tons of humid peat daily. That factory commenced to work in 1908 by utilizing 350 tons of peat placed at its disposal by the Prussian Ministry of Agriculture. The peat, a portion of which had been delivered as far back as 1907, and another part in the spring of 1908, after having been kept in the open air, was very wet; certain parts containing 42·47 per cent of water, others 65·70 per cent. The average percentage of nitrogen calculated on the dry sample was 1·05; the amount of ash was, on an average, 3 per cent. With the daily treatment of 45 tons of peat with 42 to 47 per cent of water, 1000 kg. (one metric ton) of dry substance yielded in the gas producer 2800 cubic metres of gas, containing 17·4 to 18·8 per cent of carbonic acid by volume, 9·4 to 11 per cent of carbonic oxide, 22·4 to 25·6 per cent of hydrogen, 2·4 to 3·6 per cent of

methane, 42·6 to 46·6 per cent of nitrogen, and only traces of oxygen. The combustible elements of the producer gases amounted, therefore, to between 36 and 39 per cent, and their calorific intensity was, on an average, 1400 calories per cubic metre. For peat, with 65 to 70 per cent of water, the percentage of carbonic acid and the volume of gas was higher, but the total amount of combustible elements fell to 28·6. Now, as the gas from blast furnaces, with 20 per cent of total combustibles, is still utilizable to drive gas engines, the gas, with 28·6 per cent of combustibles, yielded by such a wet peat might also be used to drive explosion motors, and, with greater reason, for heating. A measured sample of the normal gas, with 36 to 39 per cent of combustible elements, was taken to a 50 H.P. gas motor, fitted with a Prony brake, and it was found that for one effective H.P. it was necessary to use 2·4 cubic metres. Tar dust was almost completely absent. As 1 ton of peat yields 2800 metres of gas, that gives a yield of 1160 horse-power hours, and as the gas, escaping at 500° C., suffices to produce the steam required for the producers, and as the air-pumps and water-pumps, as well as the scrubber, require little force, one is safe in counting on a yield of 1000 horse-power hours per ton of dried peat, that is, on an amount of energy sufficient to combine 50 kg. (say 1 cwt.) of atmospheric nitrogen under the form of calcium cyanamide, CaN_2H_2, or from 16 to 20 kg. (35·2 to 44 lb.) of nitric acid.

But the agricultural utilization of peat is still more advantageous if the ammonia be extracted from the gas generated in the gas producers. If all the organic substance of the peat be gasified in a mixture of air and superheated steam, hydrogenation of the nitrogenous substances of the fuel is produced, i.e. of the peat, and this hydrogenation is so energetic that, if the gas be washed in a sulphuric acid scrubber, 77 to 80 per cent of its nitrogen is obtained as sulphate of ammonia. The peat burnt at Sodingen, which contained 1·05 per cent nitrogen, gave an effective yield of 40 kg. (88 lb.) of sulphate of ammonia per ton. A small lot of peat—gasified in the Stockton factory—which contained 2·8 per cent of nitrogen in the dry substance gave likewise, according to the experiments of Dr. Caro, as much as 110 kg. (242 lb.) of sulphate of ammonia per ton, whilst coal generally contains 1·5 per cent of nitrogen. No account was taken of the secondary products of the combustion of peat tar, for instance, which is obtained in somewhat important quantity, as well as acetic acid and wood-spirit, because time was wanting to estimate the value and importance of these by-products, and afterwards because it was thought that the gasification of peat would not develop on a large scale unless the two chief products which it yielded, motor gas and sulphate of ammonia, offered sufficient profit without it being necessary to instal complicated equipment for the treatment of the

by-products. If afterwards the treatment of the by-products appears to be profitable, it will then be time to examine them, but at the present they have not been taken into account. To finish, let us quote an arrangement for the extraction of ammonia from combustion gases, which is the subject of the American patent 816,035 of 5 March, 1907. The hot gases from the combustion products of coke ovens, etc., enter by a tube A into an apparatus containing the tubes of a refrigerator B, and from there into a second refrigerator D, by the pipe C. A pump G aspirates the cooled gases from the refrigerator D by the pipe F, and propels them into the tar separator H. The gases freed from tar return by the pipe I into the refrigerator D, and from there by the pipe K into the refrigerator B. In the refrigerators B and D the gases are reheated by the hot gases which enter by the pipe A and surround the tubes. From there the gases pass through the pipe L into an acid tower M, which is filled with coke or analogous material, on which a reservoir N delivers acid as a fine rain. The gases thus freed from their ammonia pass through a pipe O, into a refrigerator P,

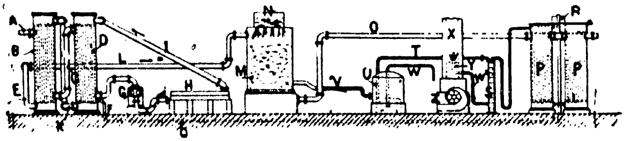


FIG. 50.—American Plant for Recovery of Ammonia from Combustion Gases.

and can then be used for different purposes. The ammonia extracted from the crude gas combined with acids, is condensed in the refrigerator D at the same time as the water. The liquid separated in B and in D is evacuated by the pipe Q into the reservoir B, and from there it is directed into a distilling apparatus S. In that apparatus it is distilled by steam along with milk of lime; the ammoniacal vapours pass by the pipe T into a saturation reservoir U, which is fed through the pipe V with liquid formed in the acid tower M. The sulphate of ammonia which is deposited on the bottom of the apparatus U is evacuated in a continuous manner by the injector W. The residuary water from the still is conducted by the pipe W′, terminated in the form of a rose, onto the chimney X, the draught of which is stimulated by the fan Z. The sulphate of ammonia thus produced contains, according to its percentage of moisture, 20 to 24 per cent of ammonia, which corresponds to 77 to 93·2 per cent of sulphate of ammonia, or to 16·5 to 19·5 per cent of nitrogen.

Crude Ammonia from Spent Oxide.—The liquid obtained from sulphate of iron and lime used for purifying coal gas, which con-

tains spent oxide, furnishes a product called crude ammonia (*crud d'ammoniac*). Although ammonia can be extracted from it in the pure state by treating it like gas liquor, generally it is simply concentrated by evaporation. A product is then obtained which should only be employed as manure with great precautions. Some years ago Maercker analysed a product of this kind, under the name of crude ammonia. He found the following products :—

TABLE LXX.—ANALYSIS OF SPENT OXIDE FROM GAS WORKS

	Per cent.	
Moisture	8·7	
Sulphate of ammonia	17·8	– 4·5 per cent nitrogen.
Insoluble nitrogen compounds	5·4	– 1·8 ,, ,,
Ferrous sulphate	15·6	
Sulphur	10·7	
Cyanogen compounds	1·2	
Ferrous oxide and ferrous sulphide	22·3	
Lime organic matter	14·8	
Sand, clay, etc.	6·3	
	100·0 containing 6·3 per cent N.	

Amongst these compounds the sulphate of ammonia is the only fertilizing material; the insoluble nitrogenous compounds, the sulphur, the lime, the sand, the clay, are inert materials; whilst the sulphide of iron and the cyanogen compounds, are plant poisons. These substances should not be employed as manure under any pretext.

Another crude ammonia of this nature, exceedingly dangerous, and also from an English source, and put on the market under the name of brown sulphate of ammonia, was analysed by C. Schuman. This product contained :—

	Per cent.	
Water	4·86	
Sulphate of ammonia	14·87	3·80 per cent nitrogen.
Sulphocyanide of ammonia	73·94 =	16·54 ,, ,,
Sand	6·23	
	99·90 with 20·34 per cent N.	

The ammonium sulphocyanide contained therein is exceedingly poisonous to plants, and before using any products of this nature it is necessary to ascertain if they are exempt from this substance.

The departmental laboratory of Châlons-sur-Marne analysed in 1907 a somewhat large number of crude ammonias from different sources. The composition of some of the samples examined is given in the following table :—

TABLE LXXI.—PERCENTAGE OF DIFFERENT NITROGEN COMPOUNDS PRESENT IN A SERIES OF SAMPLES OF CRUDE AMMONIA FROM GAS WORKS.

	Total Nitrogen. Per cent.	Nitrogen Soluble in Water. Per cent.	Ammoniacal Nitrogen. Per cent.	Nitrogen of Sulphocyanide Per cent.	Insoluble Nitrogen. Per cent.	Moisture. Per cent.
1	2·69	0·817	0·22	0	1·87	25·52
2	5·61	1·718	1·01	0·157	3·93	14·95
3	2·96	0·89	0·37	0	2·07	2·52
4	7·08	4·32	2·89	0·789	2·76	15·68
5	5·80	0·198	0·181	0·068	3·61	12·68
6	3·15	0·396	0·321	0·044	2·76	3·20
7	2·75	0·396	0·075	0·307	2·36	11·88
8	5·24	1·519	0·922	0·307	3·73	20·40
9	4·19	2·24	1·19	0·832	1·95	17·32
10	2·56	1·38	0·498	0·540	1·18	4·60
11	6·40	2·90	0·915	0·498	3·50	16·14
12	8·04	4·29	1·547	1·210	3·75	24·57
13	5·43	1·58	0·99	0·195	3·85	5·72
14	9·70	6·34	4·185	0·950	3·36	5·74
15	6·60	4·4"	2·51	1·198	2·18	10·41
16	5·60	1·58	0·697	0·535	5·02	22·67

"This table shows that the composition of these crude wastes is very irregular. There seems to be no relation between the different forms of nitrogen to be met with therein. In appearance, smell, and moisture they vary exceedingly, some black, others brown, whilst others present a whole play of colours, from deep blue to almost black, or greenish-blue. Sometimes the smell is sulphurous, sometimes cyanic, at other times the smell of benzene or tar predominates. Their consistency is generally pulverulent, sometimes, however, it is damp and pasty, and manipulated with difficulty. All these variations are explained by recalling the origin of the crude, which is a material for purifying coal gas. Ammoniacal compounds, sulphides, cyanides, come from the gas, also naphthalene and tarry matter varying in proportion according to the coal used, and also according to the arrangement of the purifiers, because efforts are made to retain the ammonia and the tar before they reach the crude. The substances used to retain the impurities are not always the classic lime and sulphate of iron (green vitriol), which yields sulphate of lime and oxide of iron; the inert absorbent, generally sawdust, sometimes consists of shavings, or again of earthy matter. The arrangement in the gas-works which delivers the waste have therefore a great influence on its composition, and this influence further increases by the care taken in storing the material after it has been removed from the purifiers.

Preparation of Ammonia Synthetically from its Elements.—The production of ammonia synthetically from a mixture of nitrogen and hydrogen was first brought about by Donkin[1] with the aid of the silent electric discharge; it has also been known for some little time that nitrogen and hydrogen could be made to unite by means of catalytic agents. Under ordinary conditions, however, the amount of ammonia produced in this way is but small and the reaction was not further studied until the matter was taken up by Haber in Germany who investigated the problem most carefully with a view to determine the conditions most favourable to the union of these two elements and thus laid the foundation of what is now one of the most important of the chemical industries. The practical development of the process was undertaken by the Badische Anilin und Soda Fabrik at Oppau near Ludwigshafen with such success that now more than 500,000 tons (some say 1,000,000 tons) of synthetic ammonium sulphate are annually produced in Germany, besides which the ammonia is oxidised to nitric acid for the production of nitrates, so that the process has helped to a very large extent to render Germany independent of any external sources of nitrates for the production of explosives, dyes, etc., and for agricultural purposes.

Notwithstanding the interest taken in this process the details have to a very large extent been kept secret, so that little information has been available; independent workers in other countries, therefore, have had to develop the methods for themselves. In a paper by Haber and Le Rossignol,[2] however, have been given some details of working with an experimental apparatus. They state that the nitrogen is preferably obtained from air by liquefaction, but it may also be produced by the alternate action of air and producer gas on heated copper. The hydrogen may be produced by the decomposition of distillation gases, by the alternate action of steam and reducing gases on heated iron, by the electrolysis of water, or by the action of water gas on calcium hydroxide.

The apparatus consists essentially of a long steel tube which contains a layer of the catalyst in the form of powder or granules, the latter being heated to the required temperature while a mixture of the two gases under considerable pressure is passed through. Temperature and pressure are most important. The most active catalyst was found by Haber and van Oordt to be manganese, but the present authors state that both osmium and uranium are far more efficient. The highest yield of ammonia in the issuing gases was obtained at a temperature of 500° C under 200 atmospheres pressure, when 18·1 per cent of ammonia was observed. This

[1] W. F. Donkin, "Proc. Roy. Soc. XXI.," 281.
[2] F. Haber and R. Le Rossignol, "Zeit. Electro-chem.," 1913, 53.

quantity is, however, exceptional. In a series of experiments with uranium as catalyst under varying pressures and temperatures, and with different rates of flow of gases, from 1·97 to 5·5 per cent of ammonia was found in the issuing gases. There seemed to be no difficulty in maintaining about 5 per cent over a lengthened period.

The ammonia is obtained from the gases by liquefaction in a refrigerating machine; a certain proportion, however, cannot thus be liquefied but remains in the gases, which are strengthened by addition of fresh nitrogen and hydrogen and again passed through the catalysis tube.

The Haber process has been the subject of a considerable amount of research in this country during the last few years, the work which has been done on these lines being described in a paper by E. B. Maxted.[1] As emphasized by him, it is necessary, in the first place, to prepare the hydrogen and nitrogen in an almost absolute state of purity, since many substances which might be present in the impure gases act as catalytic poisons and entirely prevent the reaction. Pure nitrogen is obtained from the atmosphere by liquefaction and fractionation. The liquefied product is caused to flow down a fractionating column up which passes a current of air cooled to a little above its liquefying point. In this way the oxygen of the air is condensed and flows downwards while the purified nitrogen gas passes upwards. The liquid mixture of oxygen and nitrogen falls to the bottom of the fractionating column where it is subjected to a continuous fractional distillation yielding in turn pure nitrogen and pure oxygen, the former being again admitted to the apparatus. By this method of working only about one-fifth of the air treated is actually liquefied.

With regard to the preparation of pure hydrogen, several methods have been studied but for reasons of economy electrolytic methods are out of the question. The best process appears to be the so-called continuous method in which a mixture of water gas and steam is passed over a catalytic agent, usually activated oxide of iron. By this method the carbon monoxide in the gas is replaced by hydrogen—

$$CO + H_2O = CO_2 + H_2.$$

The carbonic acid is removed from the gas by compression over water, and the small quantities of sulphuretted hydrogen, etc., which are also present, are absorbed in oxide of iron purifiers. The gas even after this treatment is not entirely free from carbon monoxide, which may be present to the extent of 1 or 2 per cent, and as this acts as a catalytic poison it is absolutely necessary that it should be removed. This residual carbon monoxide, it was found,

[1] E. B. Maxted, "Jour. Soc. Chem. Indt.," 1917, 777.

was really produced by a secondary reaction in which, at the high temperature of the catalytic furnaces, carbon is deposited from the carbon monoxide, and this again formed carbon monoxide by reacting with the carbonic acid. By a modification of the method of manufacturing the water gas sufficient carbonic acid is ensured to prevent this reaction without appreciably adding to the cost, and in this way hydrogen is prepared containing 99·94 per cent of this gas and 0·06 per cent of nitrogen, and entirely free from carbon monoxide or carbonic acid.

For the synthesis of ammonia, the nitrogen and hydrogen are mixed in the proper portions and are then submitted to considerable pressure, and while in this state the mixture of gases is passed over a heated catalyst. It has been found by experiment that very high pressures favour the production of ammonia from its elements and at the same time lower the tendency to dissociate, hence the working pressure is kept as high as possible conditional to the strength of materials and the proper working of the plant, this being 180 to 200 atmospheres. The choice of the catalyst is important since the percentage of ammonia in the exit gases is to a great extent dependent upon the catalyst used and its condition. No doubt the rare metals of the platinum group would be most efficient but they are expensive, therefore a cheaper catalyst is to be preferred. The most efficient of the latter class are uranium and iron, and although the former is the better of the two it is more difficult to prepare and also to regenerate; moreover, it is quickly rendered inactive by moisture in the gases. The iron employed is not pure but very small quantities of other elements, known as "activating" agents, are added to it. After passing through the heated catalyst the gases are cooled to − 77° C. to liquefy the ammonia, the gases being then circulated again through the apparatus. The Haber process was first installed on a commercial scale in Germany in 1913, the capacity of the plant being about 30,000 tons of ammonium sulphate per annum. In that year about 20,000 tons were actually produced. The production then rapidly increased: in 1914 it amounted to 60,000 tons, in 1915, 150,000 tons, and in 1916, 300,000 tons. In 1917 the plant was extended so that the production in that year would amount to over 500,000 tons calculated as ammonium sulphate.

Preparation of Nitric Acid by Oxidation of Ammonia.—Ammonia salts are oxidised by bacteria in the soil to nitrates, but until recently it was not possible to do this by chemical means on a large scale. The method of oxidising ammonia to nitric acid in presence of platinum was known by Kuhlmann as far back as 1830, but its practical application was only made possible in 1902 through the researches of Ostwald who employed a catalyst consisting of ordinary metallic platinum coated with platinum black, over which

a mixture of air and ammonia gas was passed at a high velocity to prevent the decomposition of the oxides of nitrogen formed as a result of the oxidation.

At the present time there are three methods of working which are essentially similar but differ in the catalyst employed. In the Ostwald process a platinum plug is now used, but the process most favoured is that in which a platinum gauze net is heated electrically. In another process base metal catalysts are employed which are "activated" by bismuth or copper. In the Ostwald process the mixture of ammonia and air is passed along a "heat interchanger" in which it comes in contact with a platinum plug. The yield of nitrate is good, averaging 90 per cent or even more, but the temperature is not so easy to regulate as in the process where platinum gauze is employed.

The production of nitric acid from ammonia has been closely studied by the Nitrates Section of the Munition's Inventions Department with considerable success, and a description of one form of catalytic converter which has proved exceptionally efficient has been given. This consists of two cones joined together by segments which are rectangular in section and of cast aluminium, provided with flanges for bolting together. Perforated baffle plates are fixed between the segments, except in the uppermost one which carries the frame on which is stretched the catalyser gauze. There is an opening in the upper cone covered with a mica window through which the catalyst can be observed while working proceeds. There is also an inlet pipe below for the introduction of the the ammonia gas and air and a corresponding pipe on the upper cone for the exit of the nitrous gases. The length of the converter is about 4 feet and its approximate weight 32 lb. Air is supplied by means of a blower, the ammonia gas being introduced into the stream through a series of nozzles, the flow of the latter being adjusted by means of a valve. It has been demonstrated, however, that better results are obtained by allowing ammonia liquor, containing about 25 per cent of the gas, to flow down a coke tower up which a current of air is driven, the mixture of ammonia and air being subsequently purified by passing it through a layer of coke or glass wool to remove any dust or oxide of iron which may remain suspended in it, the latter especially acting prejudicially on the efficiency of the catalyst.

The catalyst consists of one or more sheets of platinum wire gauze 80 meshes to the inch, of wire 0·0025 in diameter which are mounted in an aluminium frame and fixed between the upper cone and the first segment. The gauze requires a preliminary heating, which is done by electricity conveyed by leads at opposite sides attached to the wire gauze, but sufficient heat is produced during the reaction to keep the gauze at the proper temperature provided that the flow of air and ammonia is regularly maintained.

The reaction which takes place is shown in the following equation :—

$$4NH_3 + 5O_2 = 4NO + 6H_2O$$

But the greatest efficiency is attained when the proportions of air and ammonia are between those required to form N_2O_3 and N_2O_5, and nearest to N_2O_3, and the temperature between 650° and 700° C. at the gauze. When the amount of air is higher than this the temperature is too high and losses occur owing to the formation of free nitrogen, while less than this allows unaltered ammonia to pass through and the temperature of the gauze falls.

With regard to the efficiency of this converter the following figures are given: With one gauze and no external heating 90 per cent of the ammonia was converted into recoverable oxides of nitrogen, with a flow rate not exceeding the equivalent of 0·25 ton HNO_3 per sq. ft. of catalytic area per 24 hours. With two gauzes under the same conditions the yield was increased to 0·35 ton with the same efficiency, or 1·5 ton with an efficiency of 85 per cent. When the gauze is heated or the temperature of the gases is raised to 350° C. the efficiency is maintained with a much quicker flow of gases, 1·5 tons of HNO_3 per sq. ft. of catalyser area per 24 hours and with an efficiency of 95 per cent having been maintained under working conditions. The platinum gauze used weighed about 50 grams per square foot and the amount of nitric acid formed with two gauzes in position thus amounted to 15 kilograms per gram of platinum per 24 hours, which is a highly creditable performance.

After passing through the platinum gauze the hot gases, having a temperature of 400° to 600° C., are cooled as quickly as possible in a special form of cooler lined with acid-resisting materials, and issue from this at a temperature of about 30° C. More air is admitted so as to form nitrogen dioxide (NO_2). The latter may be used directly in the sulphuric acid chambers, or it is passed through a condensing tower down which water is allowed to trickle, and eventually it may be converted either into ammonium, potassium, or calcium nitrate, by neutralizing the liquors with the respective carbonates and evaporating the solutions.

Commercial Sulphate of Ammonia.—Pure sulphate of ammonia contains 25·7 per cent of ammonia or 21·2 per cent of nitrogen. Commercial sulphate contains in round numbers 20 per cent of nitrogen equal to 24·5 per cent of ammonia—the term used in Great Britain is guaranteed; however, there is generally found other salts of ammonia which bring the total up to 25 per cent. Sulphate of ammonia when pure is white, but it generally contains traces of tar or its derivatives. The yellow colour is often produced by the presence of arsenious sulphide, the green coloration by ferro cyanide of iron, but these colours disappear on drying. It is known

that ammonia is converted in the soil by bacteria into nitric acid, $NH_3 + 4O = HNO_3 + H_2O$, but this nitrification is only possible if the sulphuric acid of this salt be neutralized with lime. Commercial sulphate of ammonia should be neutral and contain as a maximum 2 per cent of water; when it contains only 1 per cent of ammonium sulpho-cyanide (NH_4CNS), it is injurious to plants, according to Maercker. But these impure products are no longer manufactured. Sulphate of ammonia is dried in a steam dryer, and if necessary crushed in ball mills with a No. 50 sieve or in Carr's disintegrator. Bags which have contained sulphate of ammonia, like nitre bags, are dried and cleaned by beating or by washing with water; the wash water in this case is returned to the concentration pan.

TABLE LXXII.—TABLE FOR CONVERSION OF NITROGEN PER CENT INTO AMMONIA PER CENT AND VICE VERSA.

Percentage of Nitrogen.	Percentage of Ammonia.	Percentage of Ammonia.	Percentage of Nitrogen.
1 × 1·214	1·214	1 × 0·8237	0·8237
2 ,,	2·428	2 ,,	1·6474
3 ,,	3·642	3 ,,	2·470
4 ,,	4·856	4 ,,	3·295
5 ,,	6·070	5 ,,	4·118
6 ,,	7·284	6 ,,	4·942
7 ,,	8·498	7 ,,	5·766
8 ,,	9·712	8 ,,	6·589
9 ,,	10·926	9 ,,	7·413
10 ,,	12·140	10 ,,	8·237
11 ,,	13·354	11 ,,	9·060
12 ,,	14·568	12 ,,	9·883
13 ,,	15·782	13 ,,	10·708
14 ,,	16·996	14 ,,	11·531
15 ,,	18·210	15 ,,	12·355
16 ,,	19·424	16 ,,	13·179
17 ,,	20·638	17 ,,	14·003
18 ,,	21·852	18 ,,	14·826
19 ,,	23·066	19 ,,	15·650
20 ,,	24·280	20 ,,	16·474
21 ,,	25·494	21 ,,	17·298
22 ,,	26·708	22 ,,	18·121
23 ,,	27·922	23 ,,	18·945
24 ,,	29·136	24 ,,	19·769
25 ,,	30·350	25 ,,	20·592

As already mentioned, the strength of sulphate of ammonia may be expressed in two ways. In France it is customary to give the percentage in nitrogen; in other countries, especially in Great

Britain, it is given as ammonia, so that the same sulphate has a strength 21·21 per cent or 25·75 per cent according to the designation adopted. To prevent any confusion, it suffices to *multiply the strength in ammonia by the number* 0·8237 *to obtain the corresponding percentage of nitrogen.* Inversely, *multiplying the percentage of nitrogen by* 1·214 *the corresponding percentage of ammonia is obtained.* The table on opposite page contains the conversion figures for all strengths met with in commerce:—

Ammonia Production.—According to the Deutsche Ammoniak Verkaufsverenigung, the world's production of sulphate of ammonia in 1910 was as follows:—

	Tons.
Germany	373,000
Great Britain	369,000
United States	116,000
France	56,000
Belgium-Holland	43,000
Austria-Hungary Spain, etc.	100,000
	1,057,000

In Great Britain the amounts were (Chief Alkali Inspector's Annual Reports.)

	1908.	1909.	1910.	1911.	1912.	1913.	1914.	1915.
Gas Works	165,218	164,226	167,820	168,783	172,094	182,180	177,930	173,675
Iron Works	18,131	20,228	20,139	20,121	17,026	19,956	16,008	15,142
Shale Works	53,628	57,048	59,113	60,765	62,207	63,061	62,749	58,826
Coke ovens, etc.	64,227	82,886	92,665	105,343	104,932	133,816	137,430	145,406
Producer gas and Carbonising Works	24,024	24,705	27,850	29,964	32,049	33,605	34,295	32,218
Total	325,228	349,143	367,587	384,976	388,308	432,618	426,412	426,267

	1909.	1910.
Exports	264,000	284,000
Home consumption	87,000	87,000

The production of ammonia in the United States, calculated as sulphate, amounted, according to W. N. McIlravy in 1909 to 106,500 tons, and in 1910 to 116,000 tons. The imports for the fiscal year ended June 30, 1908, amounted to 34,274 tons and in 1910, 62,610 tons. Altogether the home consumption of ammonia salts calculated as sulphate, therefore, amounts to about 178,000 tons.

CHAPTER XIII.

MANUFACTURE OF MANURE FROM ANIMAL WASTE.

Preliminary Remarks.—The utilization of waste of animal origin is of equal economical importance to that of human excreta. Like the latter, the products have come from the soil and been paid for in the form of manure. Unfortunately, these wastes are not collected with sufficient care, in spite of the great facility with which they can be utilized. Vast quantities of blood are annually lost in the slaughter-houses of both large and small towns, where the air is infected by the products of its decomposition. Numerous animal carcases are buried every year, not only through following an old custom, but, moreover, in order to obey certain regulations of the sanitary authorities. Conversion into chemical manure would be their best disinfection. In this conversion all animal matters are boiled, which not only destroys active organisms, but also the germs of putrefaction and the germs of contagious diseases. Moreover, as animal matters are not long in commencing to putrefy if left to themselves after boiling, manure manufacturers have the greatest interest in avoiding this decomposition, because it always entails a certain loss of nitrogen, the most valuable constituent. This is effected by drying, for dried animal matter can be stored for years without decomposing. By examining the methods used for the manufacture of manures, it will be seen that they not only afford means of making an excellent profit from animal waste, but also of destroying all the contagious germs which they may contain, and that therefore the sanitary regulations which require all animals that have died from infectious disease to be buried, are thus quite contrary to economy as well as to well-conceived hygienic measures. The animal matters rich in nitrogen most often utilized in manure manufacture are—blood, meat (flesh), horn, and leather waste.

Blood.—Fresh blood forms a red thick liquid of density 1·045 to 1·575 (6° to 7° B., or 9° to 15° Tw.). In contact with free air it soon separates into two parts, one solid, fibrous, forming the clot, whilst the other, liquid, constitutes the serum. The clot consists mostly of fibrin, whilst the serum especially contains dissolved albumen (7 to 8 per cent). Blood contains per 100 parts, 79·6 of water and 20·4 parts of solid matter. The solids consist of:—

	Per cent.
Nitrogenous matter, (fibrin, albumen, globulin)	19·1
Fat	·2
Non-nitrogenous organic	·3
Mineral matter	·8
	20·4

Amongst the mineral matters of blood, mention must be made of chloride of potassium and of chloride of sodium (common salt), and also phosphoric acid, lime, and magnesia. Phosphoric acid forms 9·8 per cent of the ash; potassium chloride, 46 per cent: corresponding to 29 per cent of potash. The composition of blood differs a little according to the animals from which it is derived, as the following analyses by Wolff show :—

TABLE LXXIII.—ANALYSES OF BULLOCKS', CALVES', SHEEP, AND PIGS' BLOOD.

	Bullocks' Blood. Per cent.	Calves' Blood. Per cent.	Sheep's Blood. Per cent.	Pigs' Blood. Per cent.
Water	79	80	79	80
Solids	21	20	21	20
Nitrogen	3·2	2·9	3··2	2·9
Phosphoric acid	0·04	0·06	0 04	0·09
Potash	0·06	0·08	0·05	0·15

Dried Blood.—Usually blood is coagulated in factories by steam in an open pan, adding to it 3 per cent of ferric sulphate solution marking 51° B. (110° Tw.). The coagulated blood is then laid to drain in perforated cases, where it remains for a month, and thus loses 40 per cent of the 80 per cent of the water which it contains. The coagulated and drained product is then dried on hot cast-iron plates in a shelf-oven traversed by hot gases. This mode of operating has numerous drawbacks; odoriferous fumes are given off by the drying itself and bad-smelling fumes owing to the partial decomposition due to irregular heating of the nitrogenous matter. Attempts have been made to remedy this, it is true, by condensing the first and denaturing the second by fire.

Moreover, not only do the arrangements necessary to secure a satisfactory result require continuous supervision, but the manufacturer does not in many cases apply them, as they perceptibly increase the cost of the products without any marked advantage as regards quality. The drying of blood in Donard and Boulet's

machine—about to be described—prevents the disengagement of all odoriferous products, and thus avoids costly gas condensation and denaturation processes. Before the application of the machine for this particular purpose, it was already in use in distilleries to dry dregs, and this use of it was described by the author as far back as 1892. The drying machine (Fig: 51) consists of a horizontal cast-iron cylinder 2·5 m. diameter by 2·5 m. long—or in round figures, 100 in. × 100 in., representing an interior volume of 12 cm. It rests on two bearings by hollow trunnions through which the heating steam enters and the evaporation steam is ejected. The heating steam enters a circular vertical steam chamber which forms the left side of the cylinder. On this side are inserted a series of horizontal tubes closed at the other extremity which form a heating surface of 59 square metres. The machine is fitted with the necessary arrangements for running off condensed water. The pivot placed at the other end of the cylinder communicates by a wide pipe with a double effect vacuum condensing pump into which the evaporation vapour passes. The cylinder is fed and emptied through two manholes. The charge of moist material—containing 55 per cent of water—is 5½ tons. It makes three revolutions a minute.

Method of Working.—The working is most simple. The machine is connected by a pipe with a tank containing the blood, then by means of the vacuum pump the air in the cylinder is rarefied so as to draw the blood in by suction. When 5½ tons have been fed into the machine, say an amount equal to ⅓ the capacity of the machine, the aspiration is discontinued and the mass is heated under a pressure of 1½ kilos whilst turning the cylinder. The blood is then perfectly coagulated under the influence of the heat without any part escaping the beating up. After one hour forty minutes to one hour fifty minutes, coagulation is complete. The apparatus is emptied, the magma being run into cloths and pressed under a press mounted on a truck. Each press will take 1 ton to 22 cwt. of dried blood as it comes from the curing machine. After a pressure of 3 kg. per sq. cm. has been applied, 400 kg. (880 lb.) of cake with 50 per cent of water are taken out; 3½ tons of these cakes are used to feed another machine absolutely identical with the first, but which this time acts the part of a drying machine. In a medium-sized factory a single machine may act both as curing and drying machine.

In factories with two machines the curer is modified by fitting two steam circulation pipes perforated in the portion which dips into the cylinder; which are used to bubble in steam during the coagulation; they have the advantage of preventing the other heating pipes from being left bare.

During the drying of the cakes a vacuum is not kept up, for the vacuum pump might draw over a portion of the extremely light

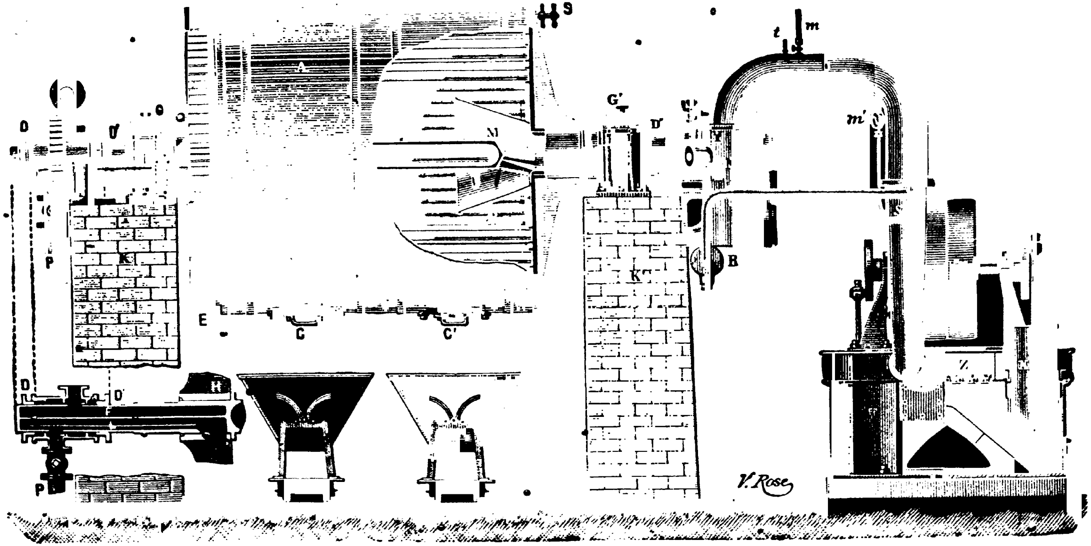


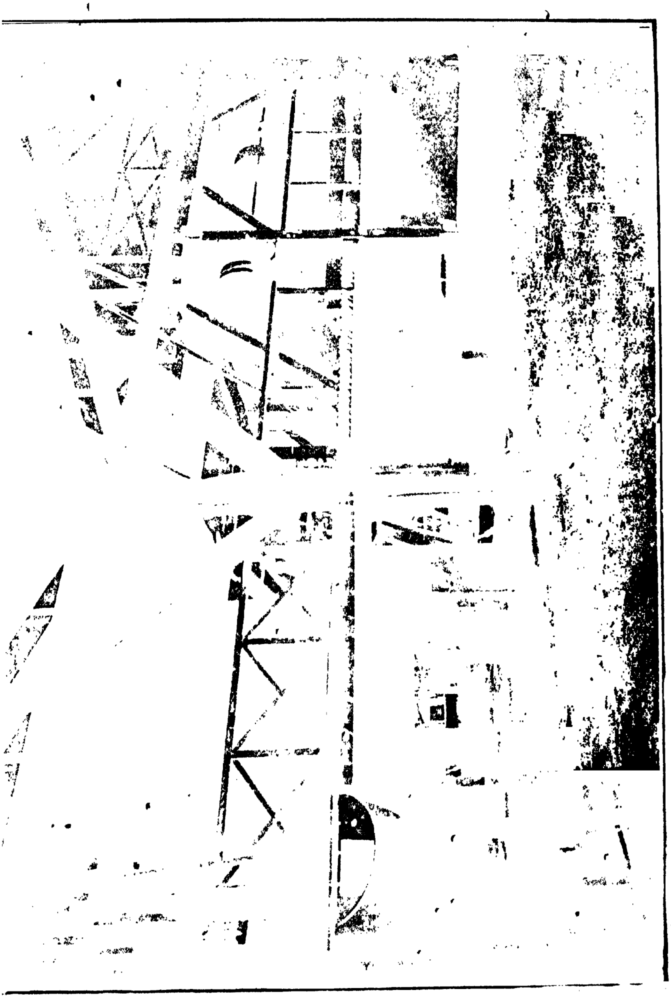
FIG. 51.—Donard and Boulet's Drying Machine.—A, Cylindrical envelope; B, Heating tubes; CC', Feeding and discharging manholes; DD', Stuffing box for entrance and exit of heating steam; D'', Stuffing box for exit of steam extracted from the material being dried; H, Entrance chamber of the heating steam, and exit of this steam when condensed, fitted with a revolving cog-wheel E; P, Exit of condensed heating steam; GG', Bearings; M, Baffle stopping entrained matter; N, Dust box; O, Pipe leading to condenser; R, Injection pipe; S, Condenser; V, Air pump; X, Piston of pump; Z, Valves; Y, Entrance tap for air; *t*, Thermometer; *mm*, Manometers; *s*, "Cheese-taster" for taking samples.

powder to which the blood is reduced by drying. During this period the vapours escape through great wooden aspirators passing through the roof. As during the process there can be no alteration of the material, either by fermentation or by superheating, the portion evaporated consists simply of pure water without trace of smell.

Drying lasts six to seven hours and induces the agglutination of certain portions into hard masses, and, to obtain an impalpable powder, the dried mass is pulverized in a Carr's crusher completely enclosed in a wooden case which is in communication with an aspirator for the recovery of dust.

The operations just described follow each other systematically. The fresh blood is converted in less than ten hours into a powder which is bagged up ready for immediate delivery. As will be seen later, 1000 litres (220 gallons or 1 ton) of blood from the Villette slaughter-houses yields with these machines 210 kg., or in round figures 4 cwt. of dried blood. As the result of several experiments made at the Aubervilliers factory, it was found that the coal used for all these conversions amounted to 0·833 lb. per lb. of dried blood. They calculate, however, that in actual practice 5 tons of coal suffice to convert 28½ tons of liquid blood. The motor power is at a maximum for three driers of 15 cubic metres each. The improvement in the yield due to these machines is considerable, as shown by the following experiment. After previously mixing 16 metric tons of blood, coagulated by ferric sulphate, and containing 62 to 65 per cent of water, was divided into two lots; the first lot of 8 tons, dried in a hot-air oven, yielded 2·555 metric tons, or a yield of 31·5 per cent. The lot of 8 tons, treated in a Donard machine, gave 3½ tons of dried blood, or a yield of 45 per cent. The percentage of water in the dried blood obtained by the two treatments was about equal, and amounted to 15 to 16 per cent. The difference of yield, 13·5 per cent, shows the loss the dried blood undergoes by overheating in the hot-air oven above-mentioned.

Meat Meal.—As far back as 1863 manure was made at Aubervilliers (Seine) from dead animals or animals slaughtered in the department of the Seine and its neighbouring departments. The fat was first extracted for the knackers and the rest was converted into manure. The flesh was cooked by steam, then pressed to extract the fat, dried, and ground. The bones were also boiled, then dried and crushed to a fine powder. Finally, with the entrails, the boilings and the residues of the organic matter, composts were made of low nitrogen content. They were mixed with the residues from the manufacture of fat, ground mineral phosphates, bone residues, fur, etc., were added, and the whole piled in a heap and drenched with blood and boilings. These substances, difficult to assimilate, especially with ground mineral phosphates, after an active and prolonged fermentation, undergo a slow conversion which renders them



assimilable. The composts mixed in different proportions with rich substances, dried meat meal, dried blood or crushed bones, enable manures of any strength to be prepared containing 1·5 to 2·5 per cent of nitrogen, and up to 25 per cent of phosphate. The mineral phosphates were coprolites. From time to time the compost heap was watered with sulphuric acid to avoid loss of ammonia and to render the phosphates soluble. The manure most rich in nitrogen so manufactured contained 12 per cent and a little phosphate. By mixing it with bone dust and alkaline salts, Dulac prepared a manure containing 8 per cent of nitrogen, 12 per cent of phosphates, 15 per cent of potash salts, soda, magnesia, etc. This manure was sold at 24 francs the 100 kg. (about £10 a ton). The Aubervilliers factory continues to use meat waste for the manufacture of manures, but it has considerably improved its processes, as will be seen. The blood in powder contains 13 per cent of water and 13·2 of nitrogen; it treats per month on an average 3500 casks of 185 litres (40·7 gallons), yielding 155 metric tons of dried blood.

Drying Blood by Lime.—Recently a simple process has been used to dry blood and to reduce it to a fine powder. This process consists in adding 1½ to 3 per cent of quicklime, which quickly converts it into a solid cake which may be dried in the air without putrefying, finally giving a fine and inodorous powder. This process has the advantage of being capable of application anywhere without any plant; moreover, it conserves 0·4 of nitrogen, which otherwise would be lost with the coagulation water. It may likewise be applied in the country by farmers, who thus possess the means of manufacturing economically an excellent nitrogenous manure.

Boiling Meat.—Butchers' waste of all sorts, skinned animals cut into pieces, are first boiled in lead-lined vats. The lid of the vat has in its fixed half a square opening to which a wooden sheath may be fitted, the other half, movable on hinges, is used to feed in the materials to be treated. Each vat is charged with—

Meat, etc.	800 kg.
Water	150 ,,
Sulphuric acid	50 ,,

The vat being charged, the lid closed, and steam turned on, the boiling lasts about twelve hours. The vertical wooden sheaths on the top of the vat form a real draught chimney branching into two large horizontal collectors which end in a masonry turret; there the vapours from the boiling are constantly precipitated by the action of a fan. The tower contains a filter of coke, constantly moistened by a stream of water. The aspirated vapours are in great part condensed owing to the freshness of this water; they then pass with it into the drain. After twelve hours the vats are opened, the

floating fat removed, amounting to 10 to 20 per cent according to the nature of the debris, then the bones and the flesh are completely disintegrated. The liquors from the boiling are drained through special pipes into two large tanks. The tallow, as it comes from the vats, is more or less coloured, according to the impurities contained in the raw material. Three classes are distinguished, white tallow, yellow tallow, and green tallow. The paler it is, the more it is valued by candle-makers and soap-makers. It is again boiled and skimmed in order to eliminate the impurities which accompany it. It is afterwards run into casks ready for delivery. After removing the tallow, that which remains in the boiler (disintegrated flesh, bones completely detached, the largest of which are removed) is put into a press which removes 15 per cent of water and is afterwards dried. The Butchers Union of Paris, in its Aubervilliers' factory, uses two systems of driers, one heated by *naked fire*, the other by *steam*. In the *steam* drier, Donard's system (Fig. 51), drying lasts seven hours at the most. The *naked fire* drier resembles an enormous coffee roaster, fitted with an agitator; it is driven by a central shaft; its furnace is arranged like that of a boiler; in this case drying lasts at least ten hours, the amount of coal consumed being enormous. Donard's dryer is much more economical and has the added advantage of yielding an absolutely inodorous powder. The drying operation is complicated by the comparatively large quantity of fat which the meat and bones retain after boiling, and which has not risen to the surface with the tallow. This fat renders the substance to be dried tacky; it is inflammable, especially when air is blown over it at a high temperature. The products coming from the dryer are brought on to a sorting sieve, which throws the bones on one side and delivers the finely powdered meat on the other side; the latter is bagged up for delivery. By the use of Donard's dryer the whole of the operations can be done in less than twenty-four hours, from the time the meat enters the factory until it is bagged up in the state of powder; 100 kg. of pressed material yield 33 kg. of dried matter; 100 kg. of pressed material correspond to 140 kg. of original material. Meat meal is sold according to its percentage of nitrogen. The following is an average analysis:—

TABLE LXXIV.—COMPOSITION OF MEAT MEAL.

	Per cent.
Water	8
Tallow	3
Nitrogen	4·6
Phosphoric acid	15

The liquors from the boiling are collected into two cisterns, where they are left to deposit for several days. The muddy deposit,

somewhat rich in organic matters, is raised by a *montejus* and poured over a very large area with raised edges, to let it drain better, then mixed with meat from the boilers or put directly into Donard's dryer. At the Aubervilliers factory 805 tons of meat, etc., are treated per month, which yields 15·8 per cent of tallow, 150 tons of dried meat, and 50 tons of bones.

M. A. Louis has organized at Caen an interesting application of Aimé Girard's process, for the destruction and disinfection of carcases and animal debris by means of sulphuric acid. Louis uses likewise slaughter-house and butchers' residues. In 1889, the first year of working, Louis made 483 tons of manure containing 16 to 18 per cent of phosphoric acid, 2 per cent of nitrogen, and 5 per cent of potash; in 1900 the production had risen to 930 tons.

Louis' method of working consists in dissolving the animal matter in sulphuric acid, and saturating the pasty mass so obtained by phosphate of lime in powder, which finally yields a nitrogenous phosphate.

Commercial Meat Meal.—The meat meal of commerce is a mixture of meat meal and bone meal. It is made from the waste from the manufacture of extract of meat in South America, also from the carcases of animals, knackers' meat, by steam heating, drying, and grinding. The greater part of the meat meal is marketed as Fray Bentos guano; it contains 6·5 to 7·5 per cent nitrogen and 11·14 to 17·18 of phosphoric acid. Finally, meat meal is rendered soluble by sulphuric acid.

Horn.—Horn is met with under different forms in commerce. The horns of ruminants are generally very pure, and contain when dry and free from bone 13 to 14 per cent of nitrogen. Whalebone waste, when not in too small fragments, is almost equal in value. Horn and whalebone turnings and shavings are less esteemed, because they are generally mixed with wood shavings and other sweepings of the workshop. Their nitrogen content rarely reaches 7 to 8 per cent. Hoofs are richer in nitrogen than ground horn. They generally consist of pure horn; on the other hand, they are often wet and soiled by excreta. Hair, wool, wool rags, old felt, and feathers have the same value as horn. But great care must be taken in buying, because it is difficult to detect the impurities of all sorts which may be mixed therein. In the pure state they contain 11 to 13 per cent of nitrogen; as sometimes delivered to the factories they contain only 5 to 6 per cent. Wool dust, from the combing and spinning of wool, is not of a nature to inspire much confidence. It rarely contains 6 per cent of nitrogen, often only 3 to 4 per cent of that element. To serve as manure all these materials must be reduced to a fine powder. But even when apparently dry they are so tenacious that it is impossible to grind them. Wool dust itself already in a fine powder cannot be ground finer. That is why they

are submitted to a special preparation, which consists in roasting them or in heating them in a closed vessel. To roast horn, it is spread on a cast-iron plate or in a shallow pan, which is heated without interruption so as to avoid overheating and loss of nitrogen. The material assumes a dark colour, and when it is cool it is brittle and easy to crush. In the case of horn turnings, it suffices to heat them for some time on the roof of a dryer. The roasting may easily be done in a closed vessel into which superheated air or combustion gases are injected. Horn is steamed in a digester. A

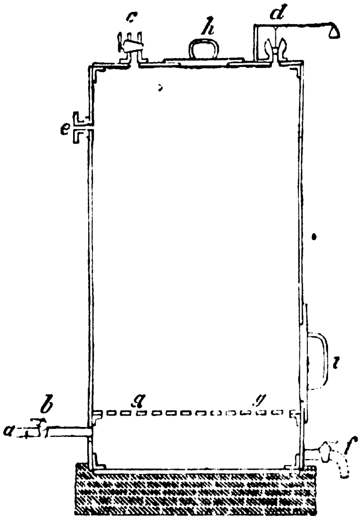


FIG. 53.—Digester for Treating Horn, Leather, etc.

digester is simply a horizontal or vertical boiler heated by steam (Fig. 53). In Fig. 53, *a* is the steam pipe fitted with a valve *b*. On the top is a steam escape valve *c*, safety valve *d*, and a short piece *e* intended for a steam gauge; *gg* is a double bottom of wrought-iron. The shape and the size of the digester vary considerably, depending on the size of the factory. However, it is well to keep to certain rules. Thus a wide somewhat low digester may usually be run cheaper, and works more economically than a tall narrow one, because it condenses less steam on its surface.

The digester being charged with horn through the manhole *h*

is closed hermetically, the steam valve *b* is opened and steam at two to three atmospheres pressure injected. It condenses at first until the whole mass is heated. The heating lasts two hours for horn in large pieces. When the operation is finished the valve *b* is closed and the apparatus left closed for some time, and finally the steam valve *c* is opened. When the pressure in the digester has fallen to almost the atmospheric pressure, the digester is emptied. To do this the liquor formed by the condensation of the steam is run off through *f*. It holds a little dissolved horn in solution; then the lower manhole *i* is opened and the horn withdrawn. When properly boiled, the horn is softened throughout, forming an elastic mass, like rubber. It is dried in a dryer, and then forms a black pliable vitreous mass which is crushed in a bone crusher; that is the way ground horn of commerce is obtained. In the pure state, it has a greenish or greyish-yellow colour, and contains 13 to 15 per cent of nitrogen. Other analogous materials are treated along with the horn. Horn shavings, wool waste, etc., occupy a great volume, and as it would require a very large-sized boiler to treat them apart, they are mixed with horn to fill the empty spaces between the larger pieces, at the risk even of slightly diminishing the percentage of nitrogen in the product. The condensed water (horn liquor) contains 1 to 2 per cent of nitrogen; it thus has a certain value, but as its treatment would be costly it is best to utilize it in the manufacture of bone dust. Attempts were made to allow it to putrefy, and then distil it to recover the ammonia, but this method was soon abandoned. The steaming of horns has many drawbacks. It requires the expenditure of much fuel and labour, and a loss of nitrogen in the condensed water. Finally, the work injures the health of the workmen. There is, in fact, disengaged from horn during the digestion a very volatile organic substance, which strongly attacks the mucous membranes, especially of the workmen engaged in emptying the digester and who consequently have to come in contact with the steamed horns, but up to the present nothing has been found to replace this method, because ground horn rendered soluble by steam is of much greater agricultural value than raw horn. It has been seen that the horn dissolves partially in the water condensed from the steam, and that without destructive decomposition it thus proves that it passes to the soluble condition at least partially. Ground horn thus rendered soluble possesses a great absorbent capacity for water, whilst ground raw horn repels water, and cannot be moistened, therefore as putrefaction requires the help of water, it follows that the soluble horn will decompose more easily, and produce a more rapid and fuller fertilizing action than raw horn. From the preceding, it will be evident that the use as manures of powdered horn and wool dust which have not been treated by steam should be abandoned, for in the raw state these materials cannot be crushed

to the requisite degree of fineness for the rational application of concentrated chemical manures.

Leather Waste.—Tanners' and curriers' waste can be bought cheap when they are unfit for glue manufacture; their nitrogen content is very variable, even when not affected by moisture or sand. Thus sole leather in the pure state and perfectly dry often contains no more than 4 to 5 per cent of nitrogen. The cuttings and waste of new leather from saddlers' and shoemakers' shops have a higher value; they contain 7 to 11 per cent of nitrogen, calculated on the dry material. Chemical manure manufacturers often treat them in the same way as horn, roasting or steaming in a closed vessel, and grinding. The roasting of tanned leather renders it friable without perceptibly modifying its chemical properties. Steaming under pressure dissolves it to a great extent. The leather liquor is sometimes so concentrated that it takes the form of gelatine, and the amount of ground leather finally obtained scarcely amounts to half of that fed into the digester. This method, therefore, is not economical. Moreover, steamed leather has only a low value as a manure, for the tannin in the tanned leather prevents the decomposition of the animal matter in the soil, and it is only partially destroyed by the heat. The powder obtained from roasted leather is even worse. It is true that the manufacturer again finds in it the greater part of the nitrogen contained in the raw material, which varies from 5 to 9 per cent. There has already been described, in discussing the preparation of bone dust, a process of preparing leather which is more advantageous both for the manufacturer and the farmer. Another method of treating woollen rags, leather waste, etc., was the subject of British patent No. 26,780 of December 22, 1905. Raw materials, such as woollen rags or leather waste, previously moistened, if need be, are fed into a horizontal cylindrical receiver in which it is treated by sulphuric acid which falls on them drop by drop, by means of a pipe running the length of the cylinder. At the same time a rotary motion is imparted to the cylinder whilst injecting hot gases from a furnace, then the materials are drenched with salt water, well mixing the whole, and continuing the heat. If leather waste be the principal raw material, it is well to add finely ground phosphate of lime to the acid water. The vapours disengaged by the material are propelled by a pump into a condensation tower lined with bricks where they are washed by a jet of finely divided water. The non-condensed gases are directed into a filter bed of moss litter, and from there escape into the atmosphere; the final product is discharged into a pit and reduced to a fine powder. By using 120° Tw. acid heated to 140° F., 4 cwt. of raw leather or 2 cwt. leather and 2 cwt. shoddy can be worked into each ton of compound manure and so well dissolved as not to be seen when the den is opened without any special method.

Comparative Value of Different Nitrogenous Manures.—Peruvian guano is the most active of nitrogenized organic manures. Popp has examined the action of the nitrogen of organic manures compared with that of nitric nitrogen. In his experiments he used every variety of organic manure, dried blood, horn dust, castor meal, ground raw bones, fish guano, meal, meat meal, Bremen poudrette and wool dust. According to the agricultural experiments which he carried out, he indicates the ratio which exists between the action of the different manures. The following are the approximate efficiency values of these manures, nitrate being taken as 100:—

TABLE LXXV.—SHOWING AGRICULTURAL VALUE OF NITROGENOUS MANURES (NITRATE = 100).

Dried blood	70
Horn dust	70
Fish guano	60
Castor meal	60
Meat Meal	60
Bremen poudrette	55
Ground bones	55
Krottnauer organic manure	45
Blankenburg manure	43
Distillery spent wash-salts	40
Wool dust	25
Concentrated cattle manure	20
Ground leather	10

The value of the dissolved organic manure is 23 per cent of that of the nitrate. Popp has, moreover, remarked that in every case the organic nitrogen is first converted into ammonia: he was not able to determine the effect of the lime. Complete conversion of organic nitrogen into nitric acid did not occur in any case. In the most favourable instance on 100 parts of organic nitrogen, 72 parts were converted into nitric acid; that is the case especially with dried blood. The nitrogen of horn dust was converted in the proportion of about 57 per cent, and the nitrogenized organic manure in the proportion of 34 per cent. Horn dust thus acted more slowly than dried blood, and the nitrogenized organic manure about half as quickly. Neither in this case was the effect of the lime in the conversion observed. In conclusion, Popp has calculated the value of the nitrogenized organic manures compared with that of nitrate of soda, the latter calculated at 35·25 francs, all expenses included. He values 1 kg. of nitrogen in such organic manures as follows:—

TABLE LXXVI.—SHOWING COMPARATIVE AGRICULTURAL MONEY VALUE OF NITROGENOUS MANURE IN FRANCS, PER KILOGRAMME.

	Francs
Dried blood	1·4
Horn dust	1·4
Fish guano	1·2
Castor meal	1·2
Meat Meal	1·2
Bremen poudrette	1·1
Bone dust manure	1·1
Krottnauer organic manure	0·9
Molasses salts	0·8
Dissolved nitrogenized organic manure	0·8
Lutzel guano	0·7
Wool dust	0·5
Concentrated cattle manure	0·4
Ground leather	0·2

Naturally these figures do not hold to-day.

CHAPTER XIV.

RECOVERY OF NITROGEN FROM DISTILLERY SPENT WASH. MANUFACTURE OF CYANAMIDE AND OF NITRATE OF LIME.

Utilization of Spent Wash.—General Remarks.—The question of the utilization of distillery spent wash, looking to its great economical importance, has engaged the attention of chemists for a long time. In grain distilleries the dregs are generally strained off and dried; the spent wash which flows therefrom contains 80 to 100 grms. of nitrogen per hectolitre; and as 100 kg. of grain yield about 3 hectolitres of liquid, the loss of nitrogen is 1 to 1·250 kg. per hectolitre of alcohol manufactured, or 1 to 1¼ lb. per 10 gal. of 100 per cent alcohol. In beet distilleries the loss in nitrogen is also very considerable; the fermented wash issuing from the distilling column containing 100 to 160 grms. of nitrogen per hectolitre. Finally, the spent wash from the distillation of molasses and saccharine liquors contains 1·4 per cent of nitrogen and 9 per cent of salts. Now, if the spent wash be simply incinerated, to extract the salts from it according to a process already old, all the nitrogen, of which the money value is greater than that of the potash, is lost. If in a molasses distillery there is a yield of 9 per cent of salts, it will be seen that there is extracted from 1000 kg. (a metric ton) of molasses 90 kg. of salts, or 198 lb., containing 40 per cent of carbonate, worth 38 centimes the degree, say 13·68 francs, or about 11s., and that there is lost by incineration all the nitrogen, of which 75 per cent at least is recoverable, say 11 kg. (22·42 lb.), worth 1·50 francs the degree, say 16·50 francs, or 13s. 2d.

It will be seen, therefore, that the problem of the recovery of nitrogen from these residues deserves the utmost attention of distillers. Different processes have been proposed for the recovery of this nitrogen. Attempts have been made to recover it by dry distillation as ammoniacal salts or liquor ammonia. There is then obtained a complex liquid containing tars, methylamines, and other substances difficult to remove. These processes have not been adopted in actual practice, which shows that the financial results did not conform with those which should be obtained to make them practically successful. Attempts were also made to prepare compound manures from spent wash by adding precipitated phosphate

of lime, and inert substances, generally lime, in comparatively large quantity up to 40 per cent. But the fertilizing elements in the products so obtained are present in proportions but little acceptable to farmers, and the presence of inert matters rendered their transport charges heavy.

The process devised by Winck to utilize the nitrogen of spent wash as manure consists in concentrating the spent wash to 40° to 42° B., then adding a quantity of sulphuric acid. This acid mixture is afterwards neutralized with carbonate of lime, and dried in stoves. The addition of acid and of carbonate facilitates the drying, while the presence of sulphate of lime renders the mass more porous, easier to deal with. The product obtained contains 3 to 5 per cent nitrogen and 12 to 14 per cent of potash. Riviere proposes to separate potash from concentrated spent wash by hydrofluosilicic acid. The organic matter separated from these salts can be evaporated in the same way as in the Vasseux process described below. Effront has likewise introduced a process for separating the organic nitrogen from the mineral substance. This process is based on the observation that the nitrogenous matter of spent wash becomes insoluble when it is treated with acid at a temperature of about 200° C. To the concentrated spent wash acid is added to decompose the organic salts; the mixture being maintained for some hours in stoves at 190° C. A portion of the nitrogen is disengaged and is collected by a fan in the acid. The mass issuing from the stove is crushed, then lixiviated with boiling water. The cooled liquid deposits sulphate of potash. The insoluble residue is dried at 100° C. By this method a product containing 8 to 9 per cent of nitrogen and free from potash is obtained.

Recovery of Nitrogen by Vasseux's Process.—By this method all the nitrogen freed from the greater part of the potash is easily recovered, no noxious products being generated in the process, which is as follows: The spent wash, previously concentrated to 32° to 35° B., is treated with sufficient sulphuric acid to convert the organic salts of potash into sulphates. The sulphate of potash formed crystallizes from the mass; it is separated by decantation, filtration, and centrifuging. This sulphate of potash is afterwards washed and again centrifuged. It is then sufficiently pure and is sold as 75 to 80 per cent sulphate. The organic matters which form the drainage are then dried in special vacuum machines; decomposition is avoided and from the distillate glycerine, tar, etc., may be collected.

When drying is complete the mass is run into trucks. It is fluid when hot but soon cools into a mass which is broken up in a crusher. An organic manure is thus obtained containing 6 to 7 per cent of nitrogen and 6 to 7 per cent of potash. This product, almost entirely soluble in water, nitrifies very rapidly in the soil and suits all

crops. For every 1000 kg. (metric ton) of molasses treated 150 kg. of this manure are recovered (in round numbers 3 cwts. manure per ton of molasses):—

TABLE LXXVII.—SHOWING VALUE AND AMOUNT OF MANURE FROM 1 TON MOLASSES.

1000 kg. (1 metric ton) of molasses yield

	Fr.
150 kg. (3 cwts.) of organic manure with 6 to 7 per cent nitrogen and 6 to 7 per cent of potash	16·60
75 to 80 kg. (165 to 176 lb., say 1½ cwt.) of sulphate of potash .	14·0
Total	30·60

whilst by the old process only 90 kg. potash salts, worth 13 to 14 francs, were obtained.

Labour is not heavier than at the potash furnaces and the work is less exhausting, but there is the extra expense in coal and in acid, which is valued at 5 francs (4s.) per metric ton of molasses. So that the net profit to be drawn from the application of this process over and above the potash salts usually obtained is about 12 francs, or in round figures 10s.

If these figures be applied to a factory working 20,000 tons of molasses, the value of the by-products obtained is 610,000 francs (£24,400), yielding a profit greater by 240,000 francs (£9600) than that obtained from the potash salts alone. These figures show very well the importance attached to the recovery of the nitrogen. Vasseux's process is, moreover, worked in France and Spain, giving every satisfaction.

Treatment of the Spent Wash by Biological Agents.—Jean Effront has studied a new method of treating spent wash by biological agents. The problem which he set himself was as follows: To find an active substance (enzyme) capable, in the conditions of actual practice, of converting the organic nitrogen of spent wash into ammoniacal nitrogen, the form under which it is most easily recovered. This substance, called amidase, exists in brewers' yeast. In the alcoholic fermentation the amidase of yeast and foreign ferments always accompanying industrial fermentation, does not exert any influence, owing to unfavourable conditions. It only reveals its presence when the yeast exists in an alkaline medium and in a non-vegetative condition. After numerous but very simple experiments which demonstrated to him the presence of amidase in yeast and its power of converting amides into ammonia, Effront applied his discovery to the treatment of distillery spent wash. 'This produces very large quantities of ferment which is deposited at the bottom of the vats; these ferments separated from the fermented liquid before its distillation may

be used to treat spent wash. The method of working is as follows: The spent wash issuing from the distilling column is cooled to 40° to 45° C. (104° to 113° F.), rendered alkaline by lime, soda, or salts. One or two kilogrammes of yeast are added per hectolitre and allowed to act for 3 or 4 days at 40° to 45° C. The conversion of amides being finished, the ammonia is separated by distillation or by ventilation (Kestner method). By this latter method the consumption of coal is about 50 kg. (about 1 cwt.) per 100 hectolitres (2200 gal.) treated. By treating molasses spent wash, 100 hectolitres (2200 gal.) yield 40 to 45 kg. (88 to 99 lb.) of nitrogen, representing a minimum value of 40 to 45 francs (32s. to 36s.). In spent wash from beets 100 hectolitres (2200 gal.) yield 10 to 15 kg. (22 to 33 lb.) of nitrogen, worth 10 to 15 francs (8s. to 12s.). The expense in fuel being 1 franc (9·6d.), the profit is therefore phenomenal.

Treating Spent Wash by Fermentation.—Beer yeast is not the only biological agent capable of converting the nitrogen of spent wash into ammonia. Certain soil organisms likewise possess this property. By inoculating a solution of glutamine with garden soil, the formation of ammonia can be demonstrated. Effront, using plate cultures, has isolated three organisms which will act on the nitrogen of spent wash. One of them was recognized as the butyric acid ferment, and Effront has closely examined the conditions which favour its ammoniacal functions. In practice the method of using this ferment is analogous to that of the manufacture of alcohol. A yeast chamber and fermentation vats being employed; from the ferment there is prepared a leaven equal to 5 to 10 per cent of the total volume of the liquid to be fermented, and it is renewed every twenty-four hours as in distillery brewing. To strengthen the ammoniacal action, recourse is made to aeration; the liquid should be rendered strongly alkaline, and the use of agglutinants, such as sulphate of alumina, which paralyses the development of ferments and produces a change in the function of the cells, is beneficial. In place of pure cultures, often far from convenient, garden soil which may be very well taken as the point of departure of ammoniacal fermentation, may be substituted. Effront recommends to sterilize this earth mixed with the alkaline spent wash for an hour at 70° to 80° C. (158° to 176° F.), this sterilization being sufficient to avoid the formation of undesirable ferments without destroying those having an ammoniacal function. This soil culture in the spent wash may be used as leaven in the same way as those made from pure cultures on condition that it be renewed somewhat frequently. This process was experimented on at the distillery of Quesnoy-sur-Deule, at the end of the season 1907-8. With regard to the yield, the work leaves nothing to be desired, the amount of nitrogen extracted from the spent wash from the manufacture of

one hectolitre (22 gallons) of alcohol, being 12 kg. (26·4 lb.) of sulphate of ammonia (or 1·2 lb. of sulphate of ammonia per gallon of alcohol). In the course of the molasses season, 25 to 30 kg. (55 to 66 lb.) of sulphate of ammonia were obtained per hectolitre of alcohol, and it has been found that, in the distilling column an appreciable amount of glycerine easily recoverable is also separated. In treating spent wash by fermentation, almost all the organic matters, including the nitrogenous matter, are decomposed. The spent wash from 370 kg. (814 lb.) of molasses, the approximative quantity required to produce 1 hectolitre (22 gallons) of alcohol, yields besides ammonia about 35 kg. (77 lb.) of volatile fatty acids. The acids which pass over on distillation are white and free from impurities. The distillery industry could furnish enormous quantities, and it would be desirable for the trade to find new outlets for them.

The Manufacture of Cyanamide and of Nitrate of Lime.—Atmospheric air is an inexhaustible source of nitrogen. It is calculated that the column of air which covers a hectare (2·47 acres) of ground contains about 79,000,000 kg. of nitrogen (say 79,000 metric tons, which is equal to 31,600,000 kg. per acre), equivalent to 500,000,000 kg. of nitrate of soda (say 500,000 metric tons per hectare or 200,000 tons per acre). But nitrogen exists in the free state in the air, and to render it assimilable by plants, it is necessary to convert it into appropriate compounds. We know that this conversion can be effected by certain bacteria of the soil (leguminous bacteria, etc.), likewise by certain phenomena which occur in nature, such as electrical discharges, especially lightning. But the amount of nitrogen brought into the soil in this way is far from being sufficient to cover the requirements of plants, and vigorous efforts are now being made to convert atmospherical nitrogen into compounds which are assimilable. Experiments made enable us to affirm that such is possible. But all the tentatives made in this direction show that the industrial fixing of atmospheric nitrogen requires the use of great quantities of electrical energy. There are at present two chief methods of manufacture: (1) the Frank and Caro process, (2) the Birkeland and Eyde process. The first consists in combining atmospheric nitrogen in the dry state and deprived of its oxygen with calcium carbide, obtained by fusion in the electrical furnace of equal amounts of coal and lime. The product so obtained is termed lime nitrogen or cyanamide of calcium ($CaCN_2$), it is, however, more or less impure. The second process consists in oxidizing atmospheric nitrogen by electrical means, converting it into nitric acid, which is put into commerce as nitrate of lime with 13 per cent of nitrogen; this is somewhat similar to nitrate of soda, and like the latter is easily assimilable by plants. The two products come on the market as more or less dark dirty

grey powders, their content of nitrogen varying from 13 to 21 per cent. The following are the analyses given by Grandeau:—

TABLE LXXVIII.—ANALYSES OF CYANAMIDE (LIME NITROGEN AND NITROGEN LIME). (GRANDEAU.)

	Lime nitrogen.	*Nitrogen Lime.*
Nitrogen	20·21	20
Calcium	40·42	45
Carbon	17·18	19·5
Chlorine	—	6·5

The only difference between the two products is that the nitrogen lime contains calcium chloride which is injurious to vegetation. Calcium cyanamide decomposes in the soil, yielding ammonia

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$$

Manufacture of Cyanamide.—"Lime nitrogen" is manufactured in Italy by the Società generale per la Cianamide, the head office of which is in Rome in association with the Berliner Zyanid Gesellschaft. This company has acquired all the patents and processes relating to the manufacture of cyanamide of calcium and its derivatives. It afterwards assigned these patents for Italy and Austria-Hungary to the Società italiana per la fabricazione di Prodotti azotati, which has installed at Piano d'Orte a factory capable of producing 10,000 tons a year. It has just acquired at Almissa numerous waterfalls of a force of 50,000 H.P., which will enable it to manufacture 1,000,000 tons per annum. Manufacturing licences have been granted in France to the Société française des produits azotés at N.-D. of Briançon; to the Société Suisse near Martigny, and to the North-Western Cyanamide Co. near Odde in Norway, the head office of which is in London. A factory using a fall of water of 40,000 H.P. is in construction in America, and two others respectively of 2000 and 10,000 H.P. are in construction in Germany. The manufacture of cyanamide according to the first of these processes has just been modified by Polzenius, who adds 10 per cent of calcium chloride to the calcium carbide used so as to fix the nitrogen in the mixture at a much lower temperature [700° to 800° C. (1292° to 1472° F.)] than in the original Frank and Caro process of 2000° C. (3632° F.). The product so obtained is called "nitrogen lime" in contradistinction to the product "lime nitrogen" by the old process. But this distinction is one of pure form, for the two products have approximately the same composition. The nitrogen in these products costs 1·4 francs the kg. (about 6d. per lb.). The factory working this process is situated at Westerregeln in Germany. It is capable of producing 4000 tons of lime nitrogen per annum.

In Germany about 30,000 tons of cyanamide were produced in 1913, and it was estimated that this would be increased to 400,000

tons in 1917. E. K. Scott placed the capacity of works built an in course of erection at 250,000 tons per annum.

The mean composition of nitrolim is given by Dr. Russell as follows:—

Calcium cyanamide	63·5	Containing nitrogen 18·8
Dicyanodiamide	0·3	
Calcium oxide	24·0	
Free carbon	12·0	
Calcium carbide	0·2	
Oil	3·0	
Moisture	4·0	
Silica, iron and alumina, etc. .	3·0	
	100·0	

Owing to the fact that the nitrolim forms an extremely fine powder which causes great inconvenience during application it is usually treated with water and dried to granulate it. The calcium carbide then forms free lime which acts on the cyanamide and polymerises it to dicyanodiamide ($C_2H_4N_4$), which is poisonous to plant life, therefore the less of this product there is present the better.

The following table reproduced from the Journal of the International Institute of Agriculture, May, 1919, shows the world's production of calcium cyanamide in metric tons:—

	1918.		1917.	1916.	1915.	1914.	1913.
	Productive capacity of works completed or under construction.	Actual Production.					
Germany . .	600,000	300,000	400,000	500,000	500,000	36,000	24,000
Austria-Hungary	30,000	24,000	24,000	24,000	24,000	24,000	7,500
France . .	300,000	100,000	100,000	100,000	80,000	7,500	7,500
Italy . . .	80,000	15,000	12,300	25,105	25,292	15,556	14,982
Norway . } Sweden . }	200,000	200,000	200,000	26,409	25,000	14,670	22,110
				18,000	16,363	18,000	18,352
Switzerland .	65,000	40,000	40,000	29,500	12,500	7,500	7,500
Canada . } United States }	58,000	58,000	58,000	58,000	58,000	58,000	48,000
Japan . .	101,605	50,000	50,802	33,462	30,278	1,1171	7,000
Total Production	1,434,605	787,802	885,102	814,476	771,433	192,397	156,944

Manufacture of Nitrate of Lime.—As just mentioned, this process consists in oxidizing atmospheric nitrogen by electric means. In 1903, Prof. Birkeland of Christiania observed that the electrical discharges from the alternating current, at an average tension, dispersed in the magnetic field, which brought about the combustion of the nitrogen in the air. This process has the advantage over similar ones of requiring a much lower electric tension, say 5000 volts in place of 15,000, and furnishes much higher yields of nitric acid. The air is burnt in an electrical oven having the form of a drum. This furnace was modified and improved by Samuel Eyde. In this drum the air is submitted to a temperature of 3000° C. By rapid cooling the nitrous oxide (NO) formed in the electric flame is retained almost entirely, whilst in former processes it was in great part lost. The nitrous oxide issuing from the furnace at a temperature of 600° to 700° C. (1112° to 1292° F.) combines with the oxygen to form nitric oxide, NO_2, which is passed through a series of towers. It finally yields nitric acid of 50 per cent strength, which is saturated with lime. The mass is then heated to 450° C. (842° F.), which is its melting-point, and is then poured into cast-iron cylinders, where it solidifies slowly. In the beginning, crystallized nitrate of lime was manufactured which was difficult to use owing to its hygroscopic properties. This product melted between the fingers and could thus only be used mixed with peat dust. For this reason attempts were made to produce basic nitrate of lime; but this product contains only 11·7 per cent of nitrogen, which rendered the freight charges heavy, and formed an obstacle to its sale. Lately, the partially dehydrated salt tested 13 per cent of nitrogen. The first manufactory of any importance of this product was built at Notodden in Norway. The experience acquired in that factory has induced the management of the company to increase the plant, to produce 8000 to 10,000 tons per annum. This factory is maintained by the Badische Anilin und Sodafabrik. The unit of nitrogen in nitrate of lime is sold at the same rate as the nitrogen in nitrate of soda.

Production of Nitrates Direct from the Air.—When an electric spark is passed through air a small quantity of nitric oxide is produced, which on oxidizing further gives rise to the formation of nitrous fumes which may be detected by their odour or by means of test papers. This reaction is the basis of the production of nitrates from the atmosphere, but unfortunately a large amount of energy is required to bring about the reaction, and in any undertaking on a commercial scale, cheap power is an absolute necessity in order to compete with the natural nitrate in regard to price. Hence it is that the process has been developed only in those countries where water power is plentiful and little or no restrictions are placed upon its utilization. Norway especially, but also Germany and the United

States are countries in which nitrates are produced by this means, but, although much research has been carried on in this direction in England during the war, it does not seem possible with fuel at the present price and such little water power as we possess to compete with countries such as the above which are so well endowed.

The different electrical furnaces used for the production of nitrates from the air and also the general methods of operation have been fully described by E. Kilburn Scott[1] from whose paper the following details are taken.

Birkeland-Eyde Furnace.—The Birkeland-Eyde furnace is in operation in Norway where there are thirty-two of 600 to 1000 kilowatt capacity at Nottoden and eight of 3500 kilowatts at Saaheim. The furnace is constructed of steel castings with brick-work between, forming a cylindrical chamber with a central cavity in the form of a disc. The air is forced through a pipe in the lower part of the furnace and enters into the inner chamber through a number of perforations through which it passes radially and, emerging into a circular channel just within the periphery of the furnace, it flows to the outlet pipe, through which it is removed.

Electrodes connected to an electrical generating plant are fixed in the furnace, and, the magnetic field being at right angles to these, the action of the alternating currents which flow through them is to deflect the arcs outwards into the reaction chamber. Each electrode becomes alternately positive and negative, hence the flames pass so rapidly from one side to another that the whole chamber appears to be filled with a continuous mass of flame. This sheet of flame in the 1000 kilowatt furnaces is about $6\frac{1}{2}$ ft. diameter, and in the 3500 kilowatt furnaces it is 8 ft. in diameter.

Schonherr-Hessberger Furnace.—At the Christiansund works of the Badische Anilin und Soda Fabrik there are twelve furnaces of this type, each of 450 kilowatts, and at the Saaheim works ninety-six of 1000 kilowatt power.

In this form of furnace there are four annular steel tubes set in the vertical position, the outer tube, about 3 feet in diameter, is constructed of steel plates riveted together and is lined with fire-brick. The inner tube, about 6 inches diameter, is the reaction chamber. In this is fitted a whirling electrode which forms a long arc flame up the centre of the chamber; the air is introduced through a series of tangentially arranged tubes so that it has a whirling motion imparted to it which materially helps in keeping the arc flame in the centre of the tube. The electrode at the bottom of the furnace is formed of an iron rod which is insulated from the furnace and is kept cold by a water-cooled copper gland. It is pushed up from below as it burns away and is lengthened

[1] E. Kilburn Scott, "Journ. Soc. Chem. Indt.," 1915, p. 113.

when required by screwing on fresh rods below without interfering with the working of the furnace. The upper electrode is also cooled by means of water. The furnace is about 40 ft. high, the flame in the 450 kilowatt furnace being 15 ft. long, and in the 1000 kilowatt furnace it is 20 ft. long.

Pauling Furnace.—The Pauling furnace is in operation in the nitric acid works at Gelsenkirchen, Innsbruck, Milan, Roche de Rame, France, and also in South Carolina, U.S.A.

It is fitted with two electrodes which are made to diverge so as to form a fan-shaped space between into which a blast of air is blown, thus filling the space with flame. In working this furnace it is first necessary to set the electrodes in such a position that with the voltage available the flame easily passes between; the current of air blown in then carries the flame upwards. The electrodes are of cast steel piping, each being built up of three pieces, so that when the upper one burns out the electrode can be reversed and the new one brought into operation. Along each electrode is run a thin copper blade for kindling purposes, this being set on edge so as to interfere as little as possible with the blast of air. These copper blades are brought within about 3 mm. of each other and are fed forward as they burn away. At each cycle of the alternating current a flame is struck which is blown upwards by the blast of air and then goes out, to be immediately followed by another. Part of the air is preheated and passes up through the bottom of the furnace, the other part is blown on to the top of the flame to facilitate cooling; the latter being mixed with some of the air and nitrous gas which has already been through the furnace and has been subjected to cooling. A separate Pauling furnace is attached to each phase and each furnace has two electrodes connected in series, there is also a chimney at the top for removal of the gases.

The three furnaces described are all single-phase furnaces, as distinct from the following, which is a three-phase furnace, and much more economical in its consumption of electrical energy.

Kilburn-Scott Furnace.—This is a three-phase type of furnace, being conical in shape and fitted with three electrodes of steel which are mounted in such a way that they can be swung out of the furnace when required for repairs or other purposes and can be brought back into position easily and quickly. Surmounting the furnace, and carried on cast-iron columns, is a water-tube boiler which not only serves to utilize the waste heat for generating steam but at the same time cools the gases as they emerge from the furnace and thus prevents undue dissociation.

The three-phase system results in the formation of a flame roughly in the shape of an inverted cone. The air is blown into this flame by means of an electric fan and the gases which pass

through are removed by a pipe near the top of the furnace. The efficiency of the furnace is increased by enriching the air with added oxygen, the best results being obtained when the proportion of oxygen to nitrogen is in the ratio 2 : 1.

Passing from the furnace the gases, now containing nitric oxide equal to about 2 per cent of nitric acid, are first partially cooled by traversing a nest of aluminium tubes and from these they go to the preheater where the residual heat is utilized for heating up the air passing to the furnace. Next the gases pass up a large circular tower constructed of steel plates lined with acid-proof brick, and in the time required in traversing this the nitric oxide is further oxidized to peroxide. An exhaust fan removes the gases from the tower and transfers them to the bottom of the first of the four condensing towers. Each of these towers is filled with acid-proof material laid in such a way as to break up the flow of gas as much as possible and thus bring it into very intimate contact with the condensing liquid, which is allowed to flow down it from a tank above. Pure water passes down No. 4 tower in the series, the liquor from this being pumped to the top of No. 3, and thence through No. 2 to No. 1. The counter current of gases thus meets a fairly strong solution of nitric acid while the weakest gas is subjected to the action of pure water. Acid of any strength up to 50 per cent can thus be produced at one operation. An appreciable proportion (up to as much as 20 per cent of the total), however, escapes solution in the water, even under the most favourable conditions, but this is not allowed to go to waste, since the gases are finally passed through a solution of sodium carbonate or milk of lime by which it forms mixtures of nitrate and nitrite or into caustic soda solution for the production of nitrite.

One important point in connection with the formation of nitrate or nitrite, is that without any chemical treatment the product can be obtained in an almost absolute state of purity.

The acid of 50 per cent strength from the condensation towers can readily be concentrated to a strength of 66 per cent by heat alone, or it can also be further concentrated to even 98 per cent by well-known methods such as that of H. Pauling, but for ordinary purposes, such as the production of nitrates, no further treatment is required than the saturation of the acid with a base and the evaporation of the liquid to crystallizing point. In this way sodium nitrate is obtained in Norway of such a high degree of purity that it can compete with Chilian nitrate. Ammonium nitrate could be made very readily if the process could be worked in this country, as we have an abundant supply of ammonia.

The installations working the Birkeland-Eyde process were stated in 1912 to have a capacity of 200,000 horse-power, while those under construction would add another 300,000 horse-power by

1916. Of course, great advantage is gained by employing water-power; the capital charges are greater than when steam-power is used but the cost is subsequently very low, being in Norway less than £1 per horse-power year.

With regard to the efficiency of the different electrical processes for the direct conversion of nitrogen to nitrates Dr. Eyde stated that at the Notodden factory, the output per kilowatt year is 853 to 938 kilograms (1870 to 2000 lb.) of nitrate of lime containing 13 per cent of nitrate, equivalent to 500 to 550 kilograms of pure nitric acid (1100 to 1200 lb.), but that as high as 900 kilograms (1980 lb.) of the latter had been attained. It has also been stated that the production at this factory per annum is 20,000 tons of nitrate of lime, 4000 tons of sodium nitrate, and 4000 tons of ammonium nitrate. As this factory is supplied with current from a power house containing four turbo generators, each of 10,000 horse-power, equivalent to 30,000 kilowatts, the yield amounts to 1478 lb. of nitrate of lime, 298 lb. of nitrate of soda, and 298 lb. of nitrate of ammonia per kilowatt year.

Dr. Pauling guarantees with his furnace a production of 60 grms. of nitric acid per kilowatt hour of electrical energy measured on the switchboard of the works, which means 525 kilograms (1157 lb.) per kilowatt year.

Therefore, although the single phase processes at present in use do not yield anywhere near the theoretical amount of nitric acid, it is possible to produce practically half a ton of 96 per cent acid per kilowatt year.

Maxted has made a comparison of the different methods for the fixation of nitrogen by calculating the total energy required in the processes to electrical energy.

By the arc process one kilowatt year of power will yield about 600 kilos of nitric acid or 130 kilos of fixed nitrogen.

By the carbide-cyanamide process about 2 kilowatt years, and in addition 3 to 3½ tons of coal or other fuel (or a total power equal to 2·6 kilowatt years), is required to produce 1 ton of fixed nitrogen. Therefore 1 kilowatt year will fix 380 kilos of nitrogen.

In the direct synthesis of ammonia 6½ to 7 tons of coal and coke are required in the generation of hydrogen and for the production of power required to fix one ton of nitrogen as ammonia. Converting this in terms of electric energy 1·2 kilowatt years are required to fix one ton of nitrogen, or one kilowatt year will fix about 830 kilos of nitrogen.

Agricultural Experiments with Cyanamide.—Calcium cyanamide has of late years been the subject of numerous agricultural experiments by P. Strohmer, O. Bottcher, Otto A. Stutzer and E. Wein.

It must be observed that in general calcium cyanamide neither

suits peaty or humic acid soils nor light sandy soils. On the other hand, it may be used in all loamy soils of average fertility. Owing to the formation of dicyanamide, this manure ought to be spread at least eight days before sowing and covered in afterwards in not too superficial a manner. The action of cyanamide is weaker than nitrate of soda, it is also slower than the latter. But as the unit of nitrogen is supplied cheaper by the new manure a greater amount can be used to restore the balance. Without doubt cyanamide deserves attention. According to the experiments of Remy, this manure succeeds very well on clay soils, less so in sandy soils. F. Loehnis has observed that the conversion of cyanamide into ammonia in the soil is effected by bacteria, for example, by the *B. Megatherium*, the *mycoid*, and other species in part new. We know that the conversion of ammonia into nitrate is likewise effected by bacteria, and according to the researches of G. Muntz and E. Laine, peat is an excellent means for bringing nitrifying bacteria to very great activity. For this purpose the peat is moistened with a solution of an ammoniacal salt after it has been mixed with lime to fix the nitric acid formed. From very detailed comparative experiments by P. Wagner, B. Dorsch, S. Mals and M. Popp, "Land Versucht," 1907 (Vol. LXVI, p. 285), with cyanamide and various nitrogenous manures, it follows that:—

1. *Sulphate of Ammonia* and *Nitrate of Ammonia* have not shown great differences in their mode of action.

2. *Carbonate of Ammonia* produced in loamy soils exactly the same results as sulphate and nitrate of ammonia. In sandy soils it did not act normally on the culture in pots except in a dose of 0.75 grm. applied once; stronger doses were injurious.

3. *Nitrate of Lime* acts normally up to the second dose (1·5 grms.) in loamy soil and up to the third dose in sandy soil (2·25 grms.). But from that moment there is an injurious action, especially in loamy soils. The high percentage of basic nitrate of lime and the still higher percentage of nitrate of lime produce injurious effects.

4. *Cyanamide* in a dose of 0·75 grm. once applied has given a favourable result in pots, although a little less than other nitrogenous manures of equal dose.

5. *Fish Guano* produced an average useful effect of 78, the action of nitrate of ammonia and of sulphate of ammonia being supposed to equal 100.

6. *Green Manures* have produced on sandy ground the same useful effect as fish guano does in loamy soils; they were, however, slightly less effective.

7. *Nitrate of Soda*, *Chili Saltpetre*, and *Sulphate of Ammonia* have regularly produced higher yields and a better utilization of the nitrogen than cyanamide.

The general result of all these agricultural experiments is the following:—

If the value of nitric nitrogen be expressed by 100, the value of the nitrogen in cyanamide is represented by 90. The lime nitrogen acts a little more feebly when its decomposition in the soil gives rise to the formation of dicyanamide resulting from the action of carbonic acid, humic acid, heat, and the absence of bacteria. The factors which favour the action of cyanamide are uniform distribution (fifteen days before the time of sowing), perfect mixing of the manure with the soil, sufficient moisture to the soil, a loamy soil rich in bacteria, spreading at the latest on 15th February for winter plants.[1]

Rules for the use of Cyanamide.—Immendorf has drawn up the following rules for the use of cyanamide:—

1. Cyanamide does no suit humic acid soils, in which its action is uncertain and where it may poison plants.

2. For the same reason its use is not recommended in light sandy, somewhat torpid soils, especially those with an acid reaction.

3. All other soils, especially loose friable soils, which contain enough lime and are regularly manured with farmyard dung, may be manured with cyanamide.

This new manure may be successfully applied, bearing in mind the following directions:—

(*a*) The dose to use per hectare should be from 150 to 300 kg. (330 to 660 lb., or 132 to 264 lb. per acre), equal to 30 to 60 kg. (66 to 132 lb.) of nitrogen per hectare (or 26·5 to 53·8 lb. per acre), according to the fertility of the soil.

(*b*) As the cyanamide gives off an enormous amount of dust, which is possibly the most unpleasant defect of this manure, the best thing to do, if a manure distributer be not available, is to mix it intimately with double its weight of not too moist soil and to spread it immediately.

(*c*) The spreading of the manure ought to be done eight to fifteen days before sowing, according to Frank. However, when this manure is applied to suitable soils, this delay is not to be insisted on (unless in case of too great drought); if it be spread three to four days before sowing and suitably covered in, cyanamide completely loses its properties injurious to the germination of the seed.

(*d*) It is essential to mix the manure with the surface layer of soil immediately after distribution, covering it in with the plough. Care should be taken not to spread the manure so long as the surface of the soil is humid and very hot.

[1] For a comparison of the manurial values of cyanamide see also J. Hendrick, "Jour. Soc. Chem. Indt.," 1911, p. 522.

(e) In no case should cyanamide be used as a top-dressing, at least until after the crop has been removed, for in that case it would be more injurious than useful.

Drawbacks in the Use of Nitrate of Lime.—A. Pitzewitz has communicated to the German Agricultural Society the results of experiments which he made with nitrate of lime as a manure.

"I used," he says, "in the spring of this year large quantities of nitrate of lime as much on grain crops as on beets, and I can say that from the point of view of the results, nitrate of lime has not shown itself inferior to nitrate of soda.

"Nevertheless, I will take care not to use it again, for the following reasons:—

"1. Stored for a long time in casks nitrate of lime suffers considerable loss in weight. Having left the casks from January in dry warehouses, I found at the time of spreading in April-May, 1898, an average loss by volatilization of 20 to 25 lb. per cask.

"2. It is very difficult to regulate its distribution by the drill. Nitrate of lime, moreover, has the grave drawback of enveloping the persons about or following the machine, as well as the horses, in a layer of tacky dust, so that labourers refuse to apply it. It is therefore for that reason that it is impossible to spread nitrate of lime by hand, for the hands would be injured, and the wind projecting the nitrate of lime about the body would endanger the eyesight. It is therefore necessary (1) to find a manure distributer which will obviate these drawbacks; (2) to improve the conditions of preserving the product during storage."

To obviate the deliquescent properties of nitrate of lime, it is mixed with equivalent quantities of alkaline sulphates, sulphate of potash or magnesia, or calcined kieserite. The product so formed is not more deliquescent than nitrate of soda, and forms a dry powder.

CHAPTER XV.

NITROGENIZED PHOSPHATIC MANURES.

CONCENTRATED manures containing both nitrogen and phosphoric acid in important quantities are only represented on the market under well-determined forms. Such manures have played a very important rôle in the history of agriculture. They were the starting-point of chemical manures, and it is through them that we first learned to fertilize the soil and to increase the vegetable production, otherwise than by farmyard manure. It was only afterwards that agriculture came to the large series of phosphates, potash salts and nitrogenous matter which have to-day become the indispensable factors of all rural exploitation. These manures are Peruvian guano and bones, to which were added gradually the different manures compounded from waste of animal origin described in the preceding chapters.

Peruvian Guano. Its Composition.—Like phospho-guanos already described, Peruvian guano is essentially a product of the decomposition of the excrements of sea-fowl. It has an analogous origin, but is formed in a different manner; whilst Baker guano contains scarcely 1 per cent of nitrogen with about 80 per cent of phosphate of lime, Peruvian guano has preserved almost integrally throughout centuries the nitrogenized organic matter, owing to the climatic conditions which prevail in the countries where such deposits are found. Birds' excrement (pigeons' and hens' dung) has been known for a long time to be a valuable manure; it is distinguished by great richness in nitrogen, contrary to what occurs in the case of mammals.' But the excrements of birds of prey (carnivoræ) are particularly rich in nitrogen, and the sea-birds which produce guano fall exactly into this category; in fact, whilst the dried mixture of the solid and liquid evacuations of man contain on an average 10·43 per cent of nitrogen and 3·88 per cent of phosphoric acid, the dried dung of the eagle contains 35·7 to 37·7 of nitrogen and 0·32 to 3·99 of phoshoric acid, whilst the urine of these birds, instead of being liquid like that of mammals, is thick, and thus does not penetrate into the soil but remains in the guano.

The deposits of nitrogenized guano extend over a vast surface of the West Coast of South America, the quality always varying according to the situation of the different deposits. The most

esteemed kind was that formerly collected on the Chincha Isles, well known to the ancient Peruvians, who came there to search for manure to fertilize their wheat and potato fields. But these islands are now completely exhausted, as well as those of Ballestas, Guanape, and Macabi. It is, therefore, unnecessary to describe them. However, we cannot help quoting the analyses of the samples of guano brought from these islands by Alexander von Humboldt in 1804, and of some others, because they correspond closely with the guanos now imported from these countries (see p. 291). The following are some of the distinctive characters of Peruvian guano, according to J. Girardin :—

It is a dry powder of a pale yellow or *café au lait* colour, but it becomes chocolate coloured as it ages or when it is exposed to the air; it absorbs, moreover, in the latter case much moisture, becomes heavier and adheres to the fingers. It exhales a strong putrid or ammoniacal odour which induces sneezing. It has a very sharp salt taste. It shows in bulk numerous whitish semi-hard concretions which can be crushed between the fingers, and which when exposed to the air soon slake and fall to dust, exhaling a very strong ammoniacal odour. Thrown into water, Peruvian guano soon sinks to the bottom, without anything rising; when heated it blackens, burning with a feeble flame with production of a strong ammoniacal vapour; the residue which it leaves is in the form of a white or slightly bluish porous slag; the weight of this residue varies only between very near limits, 27·5 to 35 per cent.

Triturated with powdered quicklime, Peruvian guano immediately gives off a strong ammoniacal odour. When thrown into a glass containing a concentrated solution of chloride of lime, it soon gives rise to disengagement of bubbles of gas which continue for a somewhat long period. In contact with hydrochloric acid it produces only a slight effervescence; moistened with nitric acid and dried in a porcelain capsule, it assumes a fine red colour. Finally, this guano only rarely contains silicious pebbles, and it contains only 1 to 1·5 per cent of sand; the maximum being 2·5 to 3 per cent.

In this same report Girardin gives the analyses of thirteen samples taken by himself from the bulk on board ship on their arrival in Havre. This document is so interesting that it will be useful to reproduce it here. The guanos delivered afterwards were less rich in nitrogen but richer in phosphoric acid than those which gave the old analyses. That is not surprising, as each new sample yields different results; for, on the one hand, the workmen entrusted with collecting it are not sufficiently careful, on the other hand, the deposits are continually altering under the influence of moisture, however small the rainfall in these countries. But the chemical transformation of the guano is not the same in every part of a deposit.

TABLE LXXIX.—ANALYSES OF PERUVIAN GUANO.

Composition.	According to Vauquelin and Fourcroy. Per cent.	According to Klaproth. Per cent.
Urate of ammonia	9·0	16·0
Oxalate of ammonia	10·6	—
,, ,, lime	7·0	12·75
Phosphate of ammonia	6·0	—
Double phosphate of ammonia and magnesia	2·6	—
Sulphate of potash	5·5	—
,, ,, soda	3·3	—
Sodium chloride (common salt)	—	0·50
Ammonium chloride	4·2	—
Phosphate of lime	14·3	10·00
Clay, sand, etc.	4·7	32·00
Water and organic matter	32·8	28·75
	100·00	100·00

TABLE LXXX.—ANALYSES OF PERUVIAN GUANO.

	Dark Yellow Guano (Oellacher).	Guano from Liverpool (Bartel).	Lima Guano (Voelcker).
Urate of ammonia	12·20	3·444	1·0
Oxalate of ammonia	17·73	13·351	10·6
,, ,, lime	1·70	16·360	7·0
Phosphate of ammonia	6·90	6·250	6·0
Double phosphate of ammonia and magnesia	11·63	4·196	2·6
Sulphate of potash	4·00	4·227	5·5
,, ,, soda	4·92	1·119	3·8
Common salt	0·40	0·100	—
Ammonium chloride	2·25	6·500	4·2
Phosphate of lime	20·16	9·940	14·3
Carbonate of ammonia	0·80	—	—
Humate of ammonia	1·06	—	—
Phosphate of soda	—	5·291	—
Carbonate of lime	1·65	0·600	—
Waxy matter	0·75	5·904	—
Sand and clay	1·68		—
Water	4·31	22·718	4·7
Organic matter and undetermined	8·26		32·3
	99·40	100·000	92·0

Thus, leaving out of account the superficial lamellar layer which obviously contains the most recently formed guano, a layer the stratifications of which may be compared to the annual rings formed in the trunk of a tree, three superimposed layers may be distinguished in the deposit—the superficial brown layer, the middle yellow layer, and the lower brown layer. The richest guano is that of the middle layer. That of the upper and lower beds being the poorest. This fact is easily explained by considering the incessant phenomena incidental to the formation of these kinds of deposits.

BLE LXXXI.—ANALYSES OF PERUVIAN GUANO.

	1	2	3	4	5	6
Water . . .	8·990	20·054	17·160	20·300	11·100	17·520
Sand and pebbles .	1·2000	1·250	1·000	1·190	10·400	15·400
Phosphate of lime .	24·000	24·000	24·500	28·000	25·500	37·000
Other insoluble salts	2·6000	3·000	0·500	2·700	20·700	11·238
Potash . . .	0·9648	2·319	2·894	1·061	2·180	2·162
Other soluble salts .	5·0352	2·981	4·306	0·239	0·92	1·380
Organic matter and ammoniacal salts	57·2100	46·396	49·640	46·510	29·00	15·300
	100·0000	100·000	100·000	100·000	100·000	100·000
Nitrogen per cent .	11·30	12·18	13·47	14·58	11·30	2·66
Ammonia ,, .	4·90	8·230	7·04	4·90	2·29	2·30

TABLE LXXXII.—ANALYSES OF PERUVIAN GUANO.

	7	8	9	10	11	12	13
Water . . .	18·800	12·740	15·025	19·740	21·500	15·300	18·00
Sand and pebbles .	4·300	3·710	2·245	2·280	17·700	20·000	16·00
Phosphate of lime .	40·300	18·000	31·800	34·800	35·600	11·500	33·800
Other insoluble salts	5·800	38·200	25·200	23·200	1·100	18·350	12·300
Potash . . .	2·026	0·771	0·578	1·824	2·500	0·676	0·4824
Other soluble salts .	10·974	14·329	13·622	8·576	0·300	2·874	8·8176
Organic matter and ammoniacal salts	18·100	12·250	11·530	9·580	21·300	31·300	10·600
	100·000	100·000	100·000	100·000	100·000	100·000	100·0000
Nitrogen per cent .	4·48	1·28	1·82	1·09	4·82	4·12	1·250
Ammonia ,, .	1·416	0·183	0·183	0·176	0·76	traces	traces

Although rain is very rare in these countries, the surface of the deposit is nevertheless moistened more or less constantly by the mists and fogs of winter. Now, moisture by its presence alone diminishes the value of the guano of the superficial bed, besides dissolving salts of potash, ammonia, lime, and magnesia in so far as they are soluble, causing them to pass into the middle bed. To this downward transition there is a corresponding ascending transition from the lower beds. In fact, the guano of the lower bed in contact with the soil is slowly decomposing, giving off ammonia and carbonate of ammonia, which being very volatile ascend towards the surface. The two opposite currents meet in the middle zone. The dissolved earthy salts fix the ammonia, which is thus converted into stable compounds. It is, therefore, easy to understand why the middle bed is richest in nitrogen and especially in ammoniacal salts. If this transference of matter in itself sufficiently explains the great differences in composition revealed by analysis, it is not the sole cause. Peruvian guano does not consist wholly of the excrement of sea-fowl. Remains of seals and other marine animals are found in the lower beds in a good state of preservation. It is, therefore, right to assume that these islands at a previous epoch, when they were less elevated, served as a refuge to a great number of these animals, and that after they had become inaccessible to the latter owing to their volcanic upheaval they became the home of sea-fowl. This hypothesis enables us to understand why the brown guano of the lower bed is of less value; for the flesh and the decomposed bones of which it consists are not so rich in nitrogen as the birds' excrement. The composition of guano, therefore, varies according to whether it comes from the upper, the middle, or the lower bed of the deposit. The concretions (nodules) of the upper bed have a composition identical with that of the powder in which they are embedded. Their colour and their structure enable one to recognize that they have been derived from the guano of the surface bed. The concretions from the middle bed are distinguished from the surrounding mass by their colour, which is paler, sometimes almost white, and they contain a crystalline nucleus or have a crystalline structure in parts. They consist chiefly of ammoniacal salts, oxalate and carbonate, and consequently contain more nitrogen than the guano in which they are embedded. The difference may be as much as about 1·5 per cent, or even much more in the case of very pure pieces. The nodules, the analyses of which are given here, according to Karmrodt and Phipson, come undoubtedly from the middle bed. They contain :—

TABLE LXXXIII.—ANALYSES OF GUANO FROM MIDDLE BED OF PERUVIAN GUANO DEPOSITS.

	Karmrodt. Per cent.	Phipson. Per cent.
Oxalate of ammonia	41·28	—
Carbonate of ammonia	—	76·93
Urate of ammonia	4·09	—
Alkaline urates	—	1·09
Nitrogenous organic matter	10·17	—
Phosphate of potash	9·52	—
" soda	9·08	—
" ammonia	7·57	—
" lime (monacid)	—	1·14
Carbonate of lime	—	9·91
Sulphate of potash	7·49	traces
" lime	3·40	traces
Magnesia and chlorine	—	traces
Moisture	7·40	10·93
	100·00	100·00

The lower beds of the deposit consist chiefly of salts of the alkaline earths, and the aggregations which are met with have also the same composition. Sulphate of potash predominates in the nodules of these beds. The following is the analysis of one of these nodules, according to Kraut:—

TABLE LXXXIV.—ANALYSIS OF PERUVIAN GUANO NODULES (LOWER BED).

	Per cent.
Sulphate of potash	45·64
" soda	13·22
" ammonia	10·23
Oxalate of ammonia	9·14
Phosphate of ammonia (basic)	12·09
" " (monacid)	4·78
Organic matter	0·94
Insoluble matter	1·90
Water	2·06
	100·00

As observed above, the percentage of nitrogen in Peruvian guano varies between 3·76 and 9·34, it is therefore much lower than in the material collected about 1860. The Chincha islands deposits have a composition somewhat like those of the old guano, as the following analyses of the Halle experimental station show.

Analyses of the guano of different cargoes is given in Table LXXXV, p. 301. As will be seen later, guano is no longer sold except in the dissolved state. As guano, leaving its nitrogen out of

account, consists mainly of phosphoric acid, in the form of phosphate of lime, it is, most generally, insoluble in the crude state. In certain very favourable circumstances, rarely met with, it becomes soluble in the soil, owing to the nitrogenous matter with which it is mixed. But beyond these conditions, it is no more soluble than the guano from Baker's Island, and consequently it is to a large extent inactive.

TABLE LXXXV.—ANALYSES OF DIFFERENT CARGOES OF PERUVIAN GUANO.

	I. Per cent.	II. Per cent.	III. Per cent.	IV. Per cent.	V. Per cent.	VI. Per cent.
Phosphoric acid, total	8·70	11·40	9·0	9·25	8·65	10·30
Phosphoric acid soluble in water	2·65 } 7·25	4·25 } 7·95	2·15 } 6·75	2·40 } 7·30	2·55 } 7·25	5·25 } 7·05
Phosphoric acid soluble in citrate, after Petermann	4·60	3·70	4·60	4·90	4·70	1·80
Nitrogen, total	8·20	13·35	14·60	8·90	8·85	8·60
„ ammoniacal	1·95	3·05	1·85	2·40	2·65	7·20
Nitrogen, nitric	0·00	0·05	0·00	0·10	0·10	0·05
„ organic	6·25	10·25	12·75	6·40	6·10	1·35
Potash	2·10	3·05	2·45	1·95	2·30	4·25
Phosphoric acid, soluble in water and citrate, per cent., on total	83·33	69·7	75·0	79·0	83·0	68·4

Dissolved Peruvian Guano.—Under this designation the Anglo-Continental Co. deliver a special form of guano with a guaranteed percentage of 7 per cent of nitrogen, 9·5 per cent of phosphoric acid soluble in water (= 10 to 11 per cent of total phosphoric acid), and 1 to 2 per cent of potash (= 2 to 3·5 of sulphate of potash). As guano is generally loaded into ships in the bottom of the hold as ballast, a part of the cargo is naturally drenched with sea water. In the early days, importers placed this damaged portion on one side; but this ended in locking up considerable capital, and means had to be taken to unlock it. Attempts were made to dry the damaged guano and to sell it cheaply to farmers. But this method of utilizing damaged guanos had numerous drawbacks. Nothing in fact could distinguish it from the guano which had not been drenched, neither the outward appearance nor the smell, nor the chemical analysis itself, which showed the same percentage of nitrogen as normal guano.

The importers carefully considered these drawbacks. Accordingly, acting on the advice of the chemists, they attempted to improve the damaged guano by dissolving it with sulphuric acid. As the manure so treated gave good results, this method of treatment was applied to all guanos indifferently, so that for the past fifteen years 96 to 97 per cent of the dissolved guanos has been produced from non-deteriorated guano. In the later contracts between the Peruvian Government and the Peruvian Guano Co., these conditions have undergone no alteration. The process used to dissolve Peruvian guano is as follows:—

As the guano exists in big lumps in the raw state it must first of all be ground to a fine powder. As it would be idle to pass all the mass of guano through the crusher, the latter is combined with a shaking sieve to separate the powder from the big lumps, which alone are ground. The crusher also eliminates from the guano stones (granite) brought from the deposits, which when they are not too large are fixed between the bars of the machine, from which they may be removed. In this way about 1 per cent of stones is obtained, which is debited against the supplies of the guano at the purchase price.

The powdered guano thus obtained is then mixed with 22 per cent of its weight of sulphuric acid of 66° B., sp. gr. 1·84 (168° Tw.), or its equivalent of acid at 60° B. As the phosphoric acid exists as dibasic phosphate, the operation requires no plant, and is done by simple shovelling. The material is then laid in heaps, where it solidifies. When the reaction is finished, the guano is again passed through the crusher to reduce it to powder, the form under which it is put on the market. Dissolved guano contains 5 to 7 per cent of nitrogen and about 10 per cent of soluble phosphoric acid; it is sold with a guaranteed analysis.[1]

As the Anglo-Continental Guano Co. can only supply a product of uniform analysis, by carefully sorting and mixing the raw guanos and not by the addition of foreign matters, sulphate of ammonia, etc., it follows that the constant decrease in the nitrogen content of the raw guanos reacts also on that of the dissolved guano. Since 1878 the guano has been delivered uniformly with 10 per cent of phosphoric acid and 5 to 7 per cent of nitrogen, at the wish of the buyer. Dissolved guano has the considerable advantage over raw guano of acting with absolute certainty. Although the phosphoric acid of raw guano dissolves in the soil, when the temperature conditions lend themselves thereto, it is precisely this dependence upon conditions which lessens its value and renders it less useful. As the solubility of the phosphoric acid, moreover, depends on the

[1] All manures in Great Britain must be so sold to meet the requirements of the Fertilizers Act.—Tr.

percentage of alkaline salts in the guano, present-day raw guanos are much less soluble than the old Chincha guanos. Farmers were, therefore, justified up to a certain point in attributing to the old guanos, now exhausted, a characteristic specific action, not only because these guanos contained 12 per cent of nitrogen against 7 per cent in the present products, but also because the ammoniacal salts now present are insufficient to bring the phosphoric acid to a soluble condition in the soil.

By now using 100 lb. of raw guano with 7 per cent of nitrogen and 14 per cent of phosphoric acid, the same results would be obtained as formerly with 58 lb. of the old guano (containing 12 per cent of nitrogen and 12 per cent of phosphoric acid), mixed with 20 lb. of 36 per cent phosphoric acid and bone ash. It follows that the use of raw guano in these circumstances would be sheer waste of phosphoric acid. Taking it for granted that all the phosphoric acid of the old guano was soluble in the soil (which is not absolutely demonstrated), it may be asserted with certainty that only the half of the phosphoric acid in the guano of the present day is soluble. Now by dissolving the guano the farmer can utilize all the phosphoric acid present in the manure. Another advantage which dissolved guano has over raw guano, is that its nitrogen cannot be volatilized, therefore it cannot lose its nitrogen in the air. All the carbonate of ammonia is converted into sulphate, and if more could be formed it would at once be fixed by the phosphoric acid.

Finally, dissolved guano is more easily applied than raw guano; it contains neither lumps, which oblige the farmer to crush it, nor dry powder, which, when spread in stormy weather, lost itself in the neighbouring fields. Dissolved guano is in the form of a moist but not tacky powder.

Other Nitrogenized Guanos.—Amongst other nitrogenized guanos, mention must be made of Ichaboe guano (Ichaboe is an island on the West Coast of Africa). This manure has been known for a long time, but was never of very great commercial importance, because the first arrivals contained only 8 per cent of nitrogen and 20 per cent of phosphoric acid; those which followed tested less and less. Ichaboe guano approaches to some extent phospho guanos. Latterly new deposits of guano have been found on the island of Ichaboe, formed by sea-fowl, and not damaged by moisture. The percentage of nitrogen in this guano, which contains feathers and the undecomposed carcases of birds, rises to 14·4 per cent, and its phosphoric acid content to 17·6 per cent.

Other deposits of guano were discovered a long time ago on different points of the African coast, such as those of Algoa Bay, Saldanha, and those of Cape Colony. But these deposits, almost all exhausted by moisture, were not of great importance.

Seal Guano.—Seal guano has been found in several parts of the West Coast of South America, in the Bay of Ferrol, in the Lobos Isles, and in the Isle of Tortuga. These localities are even now the habitat of seals, so that they are still in process of being formed. In the Lobos Isles, the guano forms a bed 70 metres (230 feet) thick at many points; it consists chiefly of the carcases of animals, bones, fur, hair, etc., all slightly soluble substances. This guano contains much less nitrogen than true Peruvian guano; it is analogous to the guanos of the lower bed of the Chinchas deposits above mentioned.

Bat Guano.—There was formerly on the market a guano of this kind, under the name of Sarde guano. Stockhardt found in this product:—

TABLE LXXXVI.—ANALYSIS OF BAT GUANO.

	Per cent.
Nitrogen	2·05
Phosphate of lime	35·30
Alkaline salts	3·60

It consists chiefly of bat excrements mingled with the dead bodies of these animals. Bat guano is found in grottoes and rock fissures, on the shores of the Mediterranean, in Brazil, Hungary, France, and near Vesoul in Egypt. The largest deposit found up to now is that of Kolumbacz, on the Danube, which contains 4000 tons of guano.

Hungarian Bat Guano contains, according to Scheibler, 1·88 per cent of nitrogen and 11·64 per cent of insoluble phosphoric acid; it is, therefore, of small value. The guano found in the neighbourhood of Cracow is richer. It forms a brown mixture of excrements and bone debris. Analysed by Krocker, it gave:—

TABLE LXXXVII.—ANALYSIS OF HUNGARIAN BAT GUANO.

	Per cent.
Moisture	7·50
Combustible matter	75·20
Ash	17·20

Its total nitrogen content is 9·170 per cent, of which 3·60 per cent is in the form of ammoniacal salts, 0·118 per cent as nitric nitrogen, and 5·452 as urea, and other organic substances. The ash consists in part of phosphate of lime, the phosphoric acid content being 3·825 per cent.

Egyptian Bat Guano contains, according to Popp :—

TABLE LXXXVIII.—ANALYSIS OF EGYPTIAN BAT GUANO.

	Per cent.	
Urea	77·800	Average of 37 analyses : nitrogen 37 per cent (soluble phosphoric acid 7·18 per cent).
Uric acid	1·250	
Creatine	2·550	
Phosphate of soda (monacid)	13·450	
Insoluble	0·575	
Moisture	3·660	
	99·285	

This guano is not only the richest in nitrogen of all guanos found up to now, but moreover of all nitrogenized manures.

Eboli Bat Guano (province of Salerno) contains, according to Dr. G. Paris, 2·996 per cent nitrogen, chiefly nitric nitrogen. There is also found :—

TABLE LXXXIX.—ANALYSIS OF EBOLI BAT GUANO.

	Per cent.
Moisture	18·20
Organic matter	29·11
Ash	52·87
	100·18

The ash contains 20·69 per cent of phosphoric acid, of which 47·96 per cent is soluble in citrate. All these deposits are comparatively unimportant.

Conclusion.—Sixty years ago Peruvian guano completely dominated the manure market; no other artificial manure could at this epoch meet the wants of the farmer. Nitrate of soda was at that time too high in price, the manufacture of sulphate of ammonia was in its infancy, that of superphosphates was just commencing and could only maintain itself with a great struggle in presence of guano; the preparation of bone manures, although well advanced at the time, was limited in its scope by the poverty of the raw material. Under these conditions, Peruvian guano was the sole regulator of the price of nitrogen and of phosphoric acid on the international market.

To-day the situation is not the same. The improvement in the condition of manufacture in the nitrate districts enables the concessionaires to flood the European markets at prices which formerly would have been regarded as ridiculous. The production of sulphate of ammonia in gasworks pursues an ever-increasing progress. The exploration of the Pacific Ocean has led to the discovery of new islands of phosphatic guano. Enormous deposits of

phosphates have been discovered. Finally, steel furnaces furnish the farmer with large quantities of phosphoric acid in the form of basic slag. The two or 3 per cent of potash supplied by Peruvian guano is largely replaced by Stassfurt salts, Aschersleben salts, etc. This abundance of manure is very reassuring with regard to the future, and the near exhaustion of the phosphatic guanos may be contemplated without apprehension.

But it is not so with regard to nitrogen, which forms only a part of guano. For however important may be the resources of the farmer from this point of view, and although he now utilizes human excreta only to a slight extent, nitrogenous manures are nevertheless the dearest. The discovery by Hellriegel of plants capable of fixing atmospheric nitrogen through the intervention of certain bacteria, now enables the farmer to economize in nitrogenous manure. Rumpler quotes the case of a rural farm which collects 40 tons of beets to the hectare (16 tons to the acre) with a very high percentage of sugar, and using only a small amount of nitrate, by ploughing in green manures [vetches or tares] and completing their action by a strong application of superphosphate. Green manuring completed by a good dose of phosphoric acid, potash and lime, forms the manure of the future. It is likely to revolutionize all the present-day systems of farming; thus freeing the farmer from paying tribute for extraneous nitrogen. In any case it is likely to solve the problem arising from the exhaustion of guano.

Fish Guano.—Historical Review.—The sea is an inexhaustible store of fertilizing matter. Independent of its own richness, it is incessantly receiving organic and mineral matter removed from the soil or detached from the mountains by rain and storms. Moreover, it receives the human excreta which civilized towns run into the rivers. All these materials contribute to maintain the marvellous fertility of the sea. For many years the sardine fishing has been a highly important source of profit to the inhabitants of the Brittany coast, and has powerfully contributed to maintain a sailor's nursery. As far back as 1620, in the single small village of Port Louis, 4000 barrels of sardines were packed annually. Up to 1823 the only method of preserving sardines consisted in salting them and pressing them in barrels; they were thus put on the market under the name of "pressed sardines". This method of preservation was replaced in 1824 by a new process known under the name of Appert, its author. This process consists in removing the head and the viscera from the sardines, and packing the cleaned fish in tinned iron boxes, in which they are preserved in oil after having undergone a preparation known to everybody nowadays. This new method produced much waste of considerable fertilizing value. However, this debris was not at first utilized but was run into the sea, where it was entirely lost. It was not until 1847 that Demolon

conceived the idea of utilizing it as a manure. He desired first of all to use it in the raw state, but as it was received at a time when the crops had been sown, he was obliged to store it for a time, when it putrefied and became a pest to the neighbourhood. Demolon then tried to preserve it by a more efficacious and less annoying process. After having tried different means he conceived the idea of boiling it. In that way he succeeded in extracting the oil, then he dried it and reduced it into cakes which kept as well as oil cakes. In 1850 he built a factory in Newfoundland to treat there the debris left from the cod-fishing. The plant of this factory consisted of six boilers to boil the fish, sixty presses, two graters and four mills The whole was driven by four small steam engines. The fish as it came to the factory was fed into a revolving horizontal steam-jacketed pan. The steam entered through the centre of this pan heated the double jacket, and in ten minutes the fish was cooked. The door of the pan was then opened and the fish fell on to an inclined plane. The water and oil run into a reservoir, and the solid parts were pressed, enclosed in *scourtins* analogous to those used for the extraction of olive oil. The products were afterwards dried in a stove with a superficies of 900 metres (3000 ft.). Finally, the oil was run into a sufficient number of vats. When the fish debris was boiled, pressed and grated, it was placed on frames lined with cloth which were pushed through the stove, so that after half an hour the completely dried debris fell into a hopper and thence into mills in which it was pulverized. Without boiling the fish it could never be dried completely or the oil extracted. By boiling, the oil was extracted, which sufficed to pay all the costs. This manure contained 5 per cent nitrogen and 49 per cent phosphate, and was sold at 30 francs the 100 kg. (12s. a cwt., £12 a ton). But this new industry injured too many interests. Demolon and his partner were circumvented by speculators, who, once masters of the factory, found nothing more urgent to do than to demolish it. Demolon's idea was not long in being taken up again in Norway, where fish manure was made after the same process, then in America, especially at Boston, and in Great Britain, always according to Demolon's process. Jules Loreau & Co. have built at Kernevel, near Lorient, that is close to the sardine factories (sardines à l'huile), so numerous in these districts, a works where they convert into manure all the detritus coming from these factories. This debris, which consists largely of heads, cartilages and intestines, is received at the factory on tables or sloped floors which allow the brine charged with blood to drop into a pit, whence it is afterwards drawn off by a pump; there is thus a liquid and a solid portion. The liquid portion, that is the brine, mixed with a certain quantity of oil which is separated from it, is delivered to the local farmers, who utilize it to enrich their

farmyard dung and especially for fertilizing meadows. A proportion of ten to fifteen barrels to the hectare (or four to six barrels to the acre) is sufficient to produce very good crops. This manure undergoes an ammoniacal fermentation in the pit and its action on vegetation is most energetic; it should therefore only be used on moist ground, after rain, for example; on analysis it shows a proportion of 1·34 per cent of nitrogen. The fish debris after draining is lifted, made into a heap and boiled over a naked fire, when a little water is added and clear brine; the boiling lasts two hours for 400 kg. (880 lb.) of sardine heads. After boiling, the material is piled in layers between two wrought-iron plates and submitted for five hours to the action of a press, from which it issues in the form of a cake. The 400 kg. (880 lb.) yield on an average 100 kg. (220 lb.) of cake with 25 per cent of water. This cake is air-dried and then pulverized in a flatstone mill, whence it issues ready to be delivered to the farmer. A pair of flatstone mills yield 1 to 1½ tons of ground cake in twelve hours, according as the weather is more or less dry. The average composition of this manure is the following:—

TABLE XC.—ANALYSIS OF BRITTANY FISH GUANO.

Volatile matter	Water		5·00
	Organic matter	50·50	57·00
	Nitrogen	6·50	
Ash	Phosphate of lime	28·00	38·00
	Carbonate of lime and (alkaline) salts	5·50	
	Silica	4·50	
			100·00

This fish manure, which is in great part delivered to the farmer without any further treatment, is also used at Kernevel in the manufacture of compound manures and in that of phospho guano. The chief compound manure, which is sold under the name of *Breton Manure*, is merely fish cake mixed with a sort of fucus (seaweed) collected at low water. As to the phospho guano, it is manufactured by treating the crushed fish cake with sulphuric acid of 50° B. Next morning it forms a paste which subsequently dries. It is advantageously used for different crops, particularly for beets. It contains on an average 2·5 of nitrogen. In Brittany the sardine industry commences at Croisic and ends at Douarnenez; it yields about 6000 barrels of sardine heads; a barrel of 225 litres contains on an average 30,000 heads.

Manufacture of Fish Guano in Norway—At the present day fish guano is manufactured chiefly in Newfoundland and on the islands of the Norwegian coasts. The most important factories of this manure are in the Lofoten Isles to the north of Bergen. The

fishing industry, which is very important in the North Sea, and the flesh of which is sold under the name of cod, yields a very abundant raw material; the head, the fins, the intestines, etc., being utilized. Norwegian fish guano somewhat resembles steamed bone dust, although it does not occur in the same pulverulent form as the latter. The process usually employed is the same as that for making bone dust. The fish debris is steamed, dried, and ground; steaming presents certain difficulties. When the digester described on page 269 is used, the material agglutinates so that the steam cannot pass through it; steaming is therefore too strong on the edges and the material is too much degelatinized, whilst the centre escapes steaming. To remedy this drawback, the firm of M. Friedrich of Plagwitz, near Leipzig, has built a horizontal digester, a perforated cylinder revolving inside an exterior cylinder. The material to be treated is fed into the interior cylinder; it is heated by steam which is injected into the exterior cylinder; then a rotary motion is imparted to the first, the effect of which is to turn the material over continuously and to renew the surfaces in contact with the steam. The gelatinous solution is separated through a tap at the bottom of the apparatus, and it is evaporated to transform it into solid gelatine. After cooking, the material contains a rather large proportion of water, for which reason the material is dehydrated before passing it to the drying machine, by passing it through either a hydraulic press or a centrifugal machine. A greasy liquor is thus obtained which separates a little oil on standing. The dry material is crushed in the same way as bones. For some years back fish guano has been treated with sulphuric acid. It contains on an average 7·9 per cent of nitrogen and 12 to 16 per cent of phosphoric acid. The following are analyses of several Norwegian guanos:—

TABLE XCI.—ANALYSES OF NORWEGIAN FISH GUANO.

	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Water . . .	12·30	16·44	13·02	10·54	8·65
Organic matter . .	53·70	70·80	49·40	50·92	59·15
Nitrogen . . .	8·15	8·15	10·38	6·39	8·01
Calcium phosphate . .	30·50	4·61	30·26	34·44	25·64

As a matter of fact, fish guano has nothing in common but the name with the different guanos which have been described in this treatise, for it contains nitrogen in a different form and less assimilable than in guanos properly so called.

In the salmon-packing industry of North America, carried on

in the districts around the Columbia River and Puget Sound, as well as South-East and West Alaska, a very large amount of fish waste is produced, amounting in 1913 to 140,000 tons, valued at about £438,000, 120,000 tons being produced in the United States and 20,000 tons in British Columbia. The waste constitutes from 25 to 50 per cent of the original fish and in its fresh state contains: Water 64·6, nitrogen 3·02, phosphoric acid 1·59, and oil 10·43 per cent, or in the dry condition: Nitrogen 8·65, phosphoric acid 4·44, and oil 28·74 per cent. During recent years this waste has been treated for the removal of the oil and the residue has been sold for cattle feeding or for manurial purposes. The method of treatment adopted is that of steaming the material in upright cylinders, and pressing the hot material in hydraulic presses, when hard cakes are formed which are steam-dried. From five working plants the output in 1913 was 286,000 gals. of oil and 1630 tons of dried scrap. The latter had the following composition: Water 4-5, nitrogen $7\frac{1}{2}$-$9\frac{1}{2}$, phosphoric acid $5\frac{1}{2}$-12, and oil 8-20 per cent. It is suggested that in the off-season these works might also profitably treat the seaweeds which grow so abundantly on the Pacific coasts and that a blend of the two would form a very valuable compound manure.[1]

Whale Guano.—Guano is also prepared from whale debris; this product is similar to the preceding. Whale flesh contains in the fresh state about 5 per cent of nitrogen, and in the dry fat-extracted state about 14 per cent. The bones of the whale contain $3\frac{1}{2}$ per cent of nitrogen and 23 per cent of phosphoric acid.

Crab Guano approaches fish guano. It is prepared from a species of sea-crab or lobster, of which there is enormous consumption on the coast of the North Sea. They are steamed, the substance pressed, then it is roasted on plates, and finally reduced to fine powder by grinding like fish guano. It is in the form of a bright yellow powder mixed with fragments of shells, and contains on an average 8 per cent of nitrogen and 3 per cent of phosphoric acid. There is also a manufactory of crab guano at Oporto, Portugal.

In other fishing industries large quantities of offals are also produced which in many cases are dried and sold as fish scrap for feeding purposes or the oil is extracted and the residue converted into manure. In the Menhaden fishing industry, for instance, which is followed along the Atlantic coast of the United States, in the neighbourhood of New Jersey, the fish, which are about the size of a herring, are first steamed and then pressed for the removal of the oil. From the press the residue falls on to a

[1] J. W. Turrentine, "U.S. Dept. of Agric., Bureau of Soils," Bull. No 150, Jan., 1915.

conveyer which delivers it into the drying room. The hot air drier for drying the fish scrap is almost universally employed. It consists of an iron cylinder about 6 ft. diameter and 30 to 40 ft. long, lagged on the outside with a non-conducting coating. It is provided with a series of iron flanges or baffles running the whole length of the cylinder, which are for the purpose of lifting the scrap and dropping it through the hot air. The cylinder is rotated on a central axis by means of an electric motor, while a current of hot air is driven through by means of a fan. The wet fish scrap is charged in at one end of the cylinder and falls out at the other in a dry condition; it delivers into a brick chamber and is conveyed by elevators to the bagging room. The transit of the material through the drier occupies from 3 to 20 minutes, by which time the moisture is reduced to 7 per cent. The material from the cookers contains 22 per cent of dry matter and 78 per cent of water. In the press 56 per cent of oil and water are removed, leaving 44 per cent of residue containing 22 of dry residue and 22 of water.

The dried fish scrap is well known under the name of fish guano, the following being some analyses by Macadam of these products[1]:—

	Raw Fish Offal.	Fish Guanos.		
		Anchovy.	Herring.	Cod.
Moisture	50·58	8·06	6·14	6·24
Oil	15·51	—	—	—
Nitrogenous organic matter[1]	18·54	66·18	70·18	57·68
Alkaline salts	10·93	4·54	1·56	2·12
Phosphates	3·84	14·92	7·92	26·17
Carbonate of lime	0·48	3·28	3·68	6·35
Silica	0·12	3·02	10·52	1·44
	100·00	100·00	100·00	100·00
[1] Containing nitrogen = to ammonia	3·31	8·62	10·42	10·13

The most important constituents of the fish guanos are the nitrogen and phosphoric acid, but potash and lime are also present. They are, however, very variable in composition as may be seen from the fact that in nineteen samples the nitrogen varied from

[1] Ivison Macadam, "Jour. Soc. Chem. Ind.," 1888, p. 83.

1 to 11 per cent, the phosphates from nearly 8 to 34 per cent and the potash from 2 to 4 per cent. Naturally their monetary value is equally variable. The nitrogenous matters, for the most part, show considerable resistance to decomposition so that the fertilizer is one which, although slow in its action, will persist for a considerable period. It is, however, somewhat injurious to seeds and young plants in the first period of active fermentation.[1]

To appreciate the fertilizing value of the manures just described, it must be borne in mind that the greater part of their nitrogen exists not under the form of readily decomposable gelatine, but as a horny substance (chitin), which, moreover, always retains a certain amount of fat. These manures therefore act slowly, after the manner of raw bone dust; if spread in autumn they decompose sufficiently in the winter to become active in the spring, supposing always that they have not been buried too deeply. Meat meal and fish meal dissolved by sulphuric acid with equal nitrogen and phosphoric acid content are of the same value and produce the same effect as bone superphosphate; it is therefore more rational to use these manures in their soluble condition. The consumption of fish guano assumes every year a new extension. The best qualities are used to feed cattle and chickens, while the ordinary sorts are used as manure. The price in the market per 100 kilos (2 cwt.) was the following at the end of December, 1907:—

Norwegian fish guano,	8 × 12	per cent =	22·80 to 23·10 francs.
British ,, ,,	8 × 9	,, =	21·55 to 20·85 ,,
,, ,, ,,	7 × 11	,, =	17·80 to 18 ,,

It is necessary to mention that there are still a large number of nitrogenous wastes, derived from substances of animal or vegetable origin when they are damaged and otherwise unutilizable which may be used for the manufacture of manure; but as these substances rarely occur on the market in sufficient quantity, it will suffice to indicate them by giving their content of phosphoric acid and potash.

[1] "Jour. Board of Agric.," 1914, p. 688.

TABLE XCII.—SHOWING THE COMPOSITION OF NITROGENOUS MANURES.[1]

The substances contain per 100 lb.	Nitrogen. lb.	Phosphoric acid. lb.	Potash. lb.	Nitrogen in dry substance. lb.
Nitrate of soda	15·3-16·0	—	—	—
,, ,, potash	13·6-13·7	—	45·1-46·6	..
,, ,, soda and of potash	14·8-15·2	—	undetermined	
Sal ammoniac	19·6-20·9	—	—	—
Dried blood	14·0-15·0	—	—	—
Meat meal	14·5 about	—	—	
Hoof and horn dust	13-16	—	—	
Wool rags	variable	—	—	
Leather shavings disintegrated	5·9·30	—	—	—
Bullocks' hair	13·78	—	—	—
Cheese	4·53	—	—	—
Colombine	8·39	1·15	0·25	8·42
Silkworm litter 5th and 6th period	3·28	—	0·15	6·64
Beetles	3·29	0·4-0·7	—	10·000
White worms	7·92	—	—	7·92
Greaves in cakes in marketable condition	11·87	—	—	12·5-15
Fish waste	5-7	2·3	—	7·6
Nitrate of soda, pure	16·47	—	—	—
,, ,, potash, pure	13·86	—	46·53	—
Sulphate of ammonia, pure	21·21	—	—	—
Ammonium chloride, pure	26·17	—	—	—

[1] The nitrogen in several of these nitrogenous manures is more than usually high, almost double that of ordinary commercial samples, e.g. meat meal, greaves, etc. No table like this is a guide to the composition of any given sample on the market, the real value of which actual analysis can alone decide. —Tr.

CHAPTER XVI.

POTASSIC MANURES.

Preliminary Remarks.—The ash of plants consists partly of carbonate of potash, the caustic and detergent properties of which were bound to attract attention from the very beginning of civilization. And as a matter of fact the ancients knew this substance and employed it in domestic economy as well as in industry. Aristotle described the manner of extracting potash from the ash of plants as practised in his day, the process being still in use in certain countries. It consists in submitting the ash to a series of washings with water, concentrating the lye by evaporation, and in calcining the residual salt. As plants leave only a small amount of ash, and as this does not wholly consist of carbonate of potash, it is clear that the yield of potash cannot be very great. The plants the most rich in potash are the following:—

TABLE XCIII.—POTASH CONTENT OF VARIOUS PLANTS.

Potash in 1000 parts.		Potash in 1000 parts.	
Pine	0·45	Fern	6·26
Poplar	0·75	Reeds	7·22
Beech	1·45	Maize stalks	17·50
Oak	1·53	Sunflower stalks	20·00
Willow	2·85	Chrysanthemum	25·00
Alder	3·90	Nettle	25·03
Wheat straw	3·90	Vetches (tares) stalks	27·50
Thistles	5·00	Absinth stems	73·00
Vine	5·56	Fumitory	79·00
Barley straw	5·80		

In this category some plants will be remarked as very rich in potash, such as fumitory and absinth. Several attempts have been made, especially about the year 1850, to cultivate them to extract the potash. Thus, in Sardinia, a plant was cultivated called in common language *glacialo* (Mesembryanthemum cristallineum) for the purpose of obtaining potash by burning it. The analysis of the ash of

this plant, cultivated in *le Nord*, showed it to contain 30 per cent of carbonate of potash and 6 per cent of carbonate of soda, and sodium chloride. To appreciate the economic bearing of this idea, it will suffice to recall that plants can only draw potash from the soil, and that by growing plants which need much potash too often on the same ground it would soon become exhausted and sterile, unless the amount of potash extracted by the plants were restored. But then that would be proceeding in a vicious circle: furnishing potash to the soil, as say potassium chloride, only to convert it into carbonate of potash in the plant which must be extracted by burning. It is unnecessary to dwell further on the subject.

Until comparatively recently plants were the sole source from which potash could be obtained, and as the industrial consumption of this product was formerly much greater than to-day (they did not then know that soda could replace potash in most of its applications), the supply was always insufficient to meet the wants of industry.

About the end of the eighteenth century the invention of Leblanc, which consisted in extracting soda from common salt (chloride of sodium), came to deliver the farmer from the incalculable tribute which he was obliged to pay annually to industry under the form of potash. Some industries, however, especially glass manufacture, continue to use potash owing to the impossibility of their replacing it entirely by soda. Attempts were subsequently made to reduce the potash which occurs in abundance in a great number of insoluble and difficultly soluble minerals such as granite, porphyry, potash-felspar with 16·6 per cent of potash. But soon the discovery and the exploitation of the enormous deposits of potash salts of Stassfurt rendered these exertions useless. For some little time potash, or better carbonate of potash (for the word potash is no longer used except to denote the impure product), has been made in considerable quantities by the Leblanc process. The raw material used being the kainit, or hard salt (p. 318), supplied by the Stassfurt mines.

Stassfurt Salts.—In the Stassfurt mines very soluble potash salts occur in sufficient quantity to meet the wants of industry for an indefinite period. Far from having recourse, henceforth, to the farmer for potash, industry is enabled to restore to him the enormous quantities which had been removed from the soil in the course of centuries. Encouraged by the geognostic conditions of the Stassfurt region, the first boring was begun on April 3, 1839, in the hope of finding new deposits of common salt, the production of which was insufficient in the district. In the month of June, 1843, portions of the salt were brought to the surface, and in 1851 a bed of salt 325 metres thick had been passed without reaching the bottom. The borehole was then 581 metres deep. The brine

extracted from the borehole in 1843 had a density of 1·205, and the deeper the bed was penetrated the more the density increased. The analysis of the product gave the following results:—

TABLE XCIV.—ANALYSIS OF FIRST BOREHOLE SAMPLE OF STASSFURT POTASH SALTS.

	Per cent.
Magnesium sulphate	4·01
,, choride	19·43
Potassium ,,	2·24
Common salt	5·62
	31·89

The low percentage of common salt in this product caused a deep dejection which seemed likely to put an end to the operations. But as far back as 1848 Prof. Marchand of Leipsic asserted that the bed of salt ought to be pure and that the magnesium salts must come from the upper beds of the deposits. The first pit (Von der Heydt) was commenced on December 4, 1851, and the second (Von Manteuffel) on January 31, 1852. In 1856 an exploitable bed was reached at 333 metres (1092 feet) depth.

In 1858 the government of the Duchy of Anhalt likewise caused two pits to be excavated for the working of salt, a very pure bed of rock salt being found 300 metres (984 feet) in thickness. But after a few years it was seen that the bed of rock salt was far from representing the chief value of the mine. It was observed in fact that the saline beds which covered the common salt, and from which the magnesium salts came which had been found in the depths of the bed, formed enormous deposits, and contained an important proportion of potassium chloride. This product, which was not at first utilized, was destined to become a source of great value to agriculture. In 1854 a deposit of potash salts consisting of pure potassic chloride mixed with a little common salt was also discovered at Kaluse in Galicia. In 1869 a factory was built for its exploitation, but after a few years working the crude salts brought to the surface contained only 1 per cent of potassium chloride. At the present time a deposit of kainit (see under this heading), which is much more extensive than that of Stassfurt, is being extracted. In 1870 boring operations were conducted by Baron Douglas at about 3 km. (2 miles) from Stassfurt, which resulted in the discovery of new deposits of potash salts, the working of which was soon begun. *Carnallite*, extracted from the mine and treated in the factory constructed at the working pit, is distinguished by its great purity. The enterprise was soon taken up by a limited liability company (Alkaliwerke Westerregeln), which continues to work it on a vast scale. Another exploitation of potash salts is that of

New Stassfurt. It is interesting on account of the kainit which it supplies to the farmer. At Stassfurt itself the pit Ludwig II, which had been abandoned for a long time, has been reopened for the extraction of carnallite. There are still found a little further away from Stassfurt the factories of Aschersleben at Bienenburg of Thiederhall in Brunswick, the Solvay factories at Bernburg, and the Wilhelmshall pit near Auderbeck in the neighbourhood of Halberstadt. It would be futile to study here in detail the potash salt deposits of Stassfurt and elsewhere. The reader desirous of more ample information is referred to the special treatises on the subject. But as a knowledge of the manufacturing methods about to be described presupposes a knowledge of the minerals which enter into the composition of crude potash salts, it is deemed useful to describe them briefly.

Crude Potash Salts.—1. *Carnallite* forms the chief ingredient of crude potash salts. In the pure state it is as clear as crystal, often iridescent; generally, however, it is coloured red or reddish-brown by scales of crystallized oxide of iron. Its fracture is conchoidal, density 1·65. It is rarely found in distinct crystals in nature. Carnallite crystallizes in the rhombic system. The angles of the bases are 120° and 60°. The crystals of secondary formation met with in mines rarely have a tablet form. They are more often octahedral. Sometimes great masses of carnallite crystals are found so compressed by pressure that their surfaces appear concave; the crystalline form is, however, quite distinct. Pure carnallite has the formula $KCl + MgCl_2 + 6H_2O$, and contains:—

TABLE XCV.—ANALYSIS OF CARNALLITE.

	Per cent.
Potassium chloride	26·76
Magnesium ,,	34·50
Water	38·74
	100·00

100 parts of water at 18·75° C. of (66·75° F.) dissolve 64·5 parts of the salt.

2. *Sylvine* or *Sylvinite* is a natural product resulting from the decomposition of carnallite, and consists mostly of pure potassium chloride. Freed from the common salt with which it is mixed, it has the composition represented by the formula KCl, and contains in the pure state:—

TABLE XCVI.—ANALYSIS OF SYLVINITE (PURE).

	Per cent
Chlorine	47·58
Potassium	52·42
	100

It is often colourless, rarely reddish or brown, brilliant like glass, with slightly vitreous reflection, altogether resembling rock salt, crystallizing like the latter in regular cubes with an octahedral surface. Its fracture is angular, its density is 2·025. The potash salt found at Kalusz consists chiefly of sylvine; it is coloured blue, which generally only occurs with rock salt; according to certain authors, however, this coloration is due to admixture with blue rock salt. Sylvine as it comes from the mine has the following composition, according to Mercker :—

TABLE XCVII.—ANALYSIS OF SYLVINE AS IT COMES FROM THE MINE.

	Per cent.
Potassium chloride	30·55
Sodium ,,	46·05
Magnesium ,,	2·54
Potassium sulphate	6·97
Magnesium ,,	4·80
Gypsum	1·80
Water and insoluble	7·29
	100·00

Its potash content is 23·04.

3. *Kainit* is met with in large quantities, chiefly in the Leopoldshall mine and at New Stassfurt. A deposit of more than 25 metres (82 feet) thick has been found at Kalusz of almost pure kainit. It is colourless, or yellow to reddish or even a very dark brown. It is very hard in comparison with the other minerals mentioned in this chapter. Its density is 2·131. Its fracture has a crystalline lustre; it rarely gives true crystals. It contains, according to Reichardt :—

TABLE XCVIII.—SHOWING ANALYSIS OF KAINIT. (REICHARDT.)

Potash	17·37
Soda	5·90
Magnesia	14·76
Sulphuric acid (SO_3)	30·00
Chlorine	18·56
Insoluble	0·22
	86·81
Less oxygen equivalent to the chlorine	4·18
	82·63
Water	17·37
	100·00

or

Sulphate of potash		32·12	54·99
,, ,, magnesia		22·87	
Magnesium chloride			16·95
Water			17·37
As impurities	Common salt		9·90
	Insoluble		0·22

Pure kainit responds to the formula—

$$K_2SO_4 + MgSO_4 + MgCl_2 + H_2O$$

Kainit is, therefore, a double sulphate of potassium and magnesium combined with magnesium chloride. It forms a peculiar compound, which no one has yet succeeded in reproducing artificially like sylvine and carnallite. Its mode of formation is thus uncertain; it is supposed, however, that it results from the action of water on a mixture of carnallite and kieserite found in the salt deposit. Kainit, as it is extracted in considerable quantities from the Leopoldshall, New Stassfurt and Kalusz mines, is freed as much as possible from common salt intercalated with it, then it is reduced to fine granules in a salt mill. It is put on the market as ground kainit, and contains on an average 65 to 75 per cent of pure kainit or 23 per cent of sulphate of potash (equal to 12·4 per cent of potash). The impurities consist chiefly of common salt and clay. Formerly, kainit was calcined and ground. This process has been abandoned in the Stassfurt factories. As it readily cakes and is then very difficult to break up, it has been mixed, on the advice of Fleischer, with 2·5 per cent of peat powder, which prevents this drawback. The same treatment is recommended for other potash salts when they are sold for manure.

4. *Schoenite* is the double sulphate of potassium and magnesium and responds to the formula $K_2SO_4 + MgSO_4 + 6H_2O$. Its formation, at the expense of the kainit by elimination of the chloride of magnesium, would therefore be very plausible; its existence as a mineral is not established with certainty. Artificial schoenite will be described later.

5. *Polyhalite*.—Is found in veins 26 to 33 metres thick in the deposits of rock salt. It is mostly amorphous, rarely crystalline, of a grey colour and conchoidal fracture. Density 2·72.

TABLE XCIX.—ANALYSIS OF POLYHALITE.

	Per cent.
Potassium sulphate	27·90
Magnesium "	19·76
Calcium "	42·64
Water "	5·75
Common salt and impurities	3·49
	99·54

It responds therefore to the formula—

$$K_2SO_4 + MgSO_4 + 2CaSO_4 + 2H_2O$$

When treated with water it is the potassium salt which most readily dissolves, whilst the magnesium sulphate and the calcium sulphate

remain in great part undissolved. Before being discovered in the Stassfurt mines polyhalite had been already met with in different places at Ischl, Hallein, Berchtesgaben, etc., partly as rhombic crystals or fibres or minute crystalline rods.

6. *Krugite* has a chemical composition similar to polyhalite. It responds to the formula—

$$K_2SO_4 + MgSO_4 + 4CaSO_4 + 2H_2O$$

TABLE C.—ANALYSIS OF KRUGITE. (MERCKER.)

	Per cent.
Potassium sulphate	18·60
Magnesium ,,	14·70
Calcium ,,	61·00
Water	4·20
Common salt	1·50
	100·00

Density 2·801.

It now remains to describe the processes used to extract from these minerals the whole series of products supplied to agriculture as potassic manures.

Manufacture of Potassium Chloride [muriate of potash].—The crude salt treated consists of a mixture of all the salts described above. However, carnallite predominates; forming 50 to 60 per cent of the crude salt, equal to a potassium chloride content of 13 to 17 per cent. The processes now used in the treatment of the crude salt in the manufacture of purer potash salts (potassium chloride) are based essentially on the property of carnallite to decompose in presence of water into potassium chloride and magnesium chloride; it is therefore dissolved and potassium chloride separated from the solution by crystallization. The process is in itself very simple; what complicates it is the presence of quite a series of foreign salts accompanying the carnallite, the most important of which are rock salt [NaCl], in the proportion of 20 to 25 per cent, and kieserite [$MgSO_4 + H_2O$], which forms 15 to 20 per cent of the crude salt. Other minerals, such as kainit, polyhalite, tachydrite, $CaCl_2 + 2MgCl_2 + 12H_2O$, etc., are rarely met with in large proportion but when present they are very troublesome in the process.

Crushing the Crude Salts.—As the mines deliver the crude salt in big lumps (in the beginning they delivered them ground), they must be crushed before being treated. Formerly the lumps were crushed by blows from a mallet with a long handle, but now all the factories have laid down mechanical crushers for the purpose; the machine most used is the jaw-breaker crusher already described.

Dissolving the Crude Salts.—The crushed salt is fed into a pan, in which it is dissolved. The crushed salt falls from the mill into

the receiver of a cup elevator, which delivers it directly into the dissolving pans or into a wrought-iron shoot. The elevator is driven by a shaft on which is mounted the belt pulley. The dissolving pan is of riveted wrought-iron of a cylindrical form ending in a conical bottom. At the beginning of the cone is a perforated false bottom intended to retain the residues from the salt, these residues being run out through a manhole. The solution is drawn off by a tap, the pan is steam heated. In the early days the Stassfurt and Leopoldshall factories proceeded in an appreciably uniform manner, but lately they have adopted different methods more conformable to the interests of each factory. The oldest method, still much employed, is the following: The dissolving pan is first partly charged with water, mother liquor, which is termed U, with residual solution I (see further on) and with clarified solution III (see further on). After having brought this mixture to the boil, by direct injection of steam, the crude salt is fed into the elevator, whilst continuing to boil without interruption; the carnallite soon dissolves and therefore the density of the solution increases gradually; the escaping steam, by a suitable arrangement, sets the liquid in motion and mixes its different components. When the density of the liquid, taken on a boiling sample, reaches 32° to 33° B., the elevator is stopped, the steam turned off and the solution run out; the residue remaining in the pan contains a large proportion of kieserite, common salt, and about 2 to 4 per cent of potash salts. In a great number of factories this residue is again taken up and boiled with a little water; the solution thus obtained (I) consists, therefore, chiefly of common salt with a little magnesium chloride and magnesium sulphate. Its potassium content varies from 3 to 7 calculated as potassium chloride; it is used solely to dissolve fresh quantities of crude salt. The proportions of the different solutions as well as the densities vary with the factory. The residues are thus more or less abundant and retain more or less salts. The best results are obtained by preparing solutions of 32° B., with lower densities they retain a large amount of common salt; when, on the contrary, their density is higher, they retain less common salt and more potassium chloride.

Clarification.—Crude solution as it comes from the pan is contaminated with impurities; it is therefore run into clarification basins, where it remains for about forty-five minutes. These basins are rectangular, of riveted wrought-iron, fitted with two apertures, from one of which the clarified solution is run off, and from the other the sludge. To prevent the clarified solution carrying the sludge with it, different arrangements have been made to retain it. After the clarified solution has been run off, it is led through a wrought-iron gutter into underground crystallizers. As the solution cools in flowing through the gutters, it deposits a certain amount of

salt containing 45 to 50 per cent of potassium chloride. This gutter salt is most generally used in manure manufacture, being generally treated along with potassium chloride of a higher strength.

Crystallization.—The crystallizers in which the solution cools and forms crystals of potassium chloride are of riveted wrought-iron like the clarification basins; they vary in size and shape, sometimes flat because the solution cools more quickly therein, sometimes deep because they occupy less space and yield larger crystals. When the solution is cold, which takes two to four days, the mother liquor II is decanted from the crystals of potassium chloride; it is run off by the gutters fixed under the crystallizers into wrought-iron basins or into masonry ones lined with cement. It is used either to dissolve the crude salt or treated directly, as will be described further on. The potassium salt which is deposited in the crystallizers consists of a mixture of potassium chloride and common salt, but contaminated by adhering mother liquor. It crystallizes in the same form as sylvine, with this difference that the crystals are not always perfect; their size depends chiefly on the density of the solution of crude salt from which it separates. When that has a density of 32° to 33° B., or a still weaker density, crystals, often one centimetre wide, with a pearly lustre, are obtained. When the solution is more dense, say about 33° to 35° B., it forms soft crystalline needles. It is clear that the size of these crystals must considerably affect the purity of the potassium chloride, as attenuated crystals must retain more mother liquor than large ones, and that consequently the former contain more magnesium chloride. The impure, fine, granular salt often contains only 60 per cent of potassium chloride, whilst the salt in large crystals yields on analysis:—

TABLE CI.—ANALYSIS OF CRYSTALS FROM POTASH SALT CRYSTALLIZERS.

	Per cent.
Insoluble	0·0876
Magnesium sulphate	1·2468
,, chloride	6·9072
Potassium chloride	68·1504
Common salt	23·5560
	99·9480

It may be remarked in passing that the salt that is deposited on the sides of the crystallizers is always more pure than that deposited at the bottom. To obtain high strength products, a portion of each of the two kinds may be taken, especially for continuing the treatment.

Clarifying.—As potassium chloride of 60 to 70 per cent strength

is hardly marketable, it is necessary to submit it to a further treatment—*clarification*. For this purpose it is run into vats termed clarifying vats, fitted with a double bottom covered by cloth or with a network of osiers. It is covered with water, so that the water is 2 to 3 centimetres above that of the salt, and left in contact 5 to 6 hours; then the clarified solution III is run off through a bung-hole in the bottom of the vat. This liquid runs into a special basin, from which it is removed to the dissolving pans by means of a pump. The liquid from the above clarification of 30° B. contains:—

TABLE CII.—ANALYSIS OF MOTHER LIQUOR FROM CLARIFICATION OF POTASH SALTS.

	Per cent.
Water	72·212
Magnesium sulphate	1·659
,, chloride	11·730
Potassium ,,	5·930
Common salt	8·469
	100·000

If the potassium chloride be not sufficiently enriched by a single clarification, this operation is repeated once or twice until the salt contains at least 80 per cent of dry potassium chloride. The above clarifying liquor constitutes a saturated solution. Now a solution of this nature contains at 15° C. 25 per cent KCl when it is prepared from pure potassium chloride, 27 per cent NaCl when it is made from common salt. If these figures be compared with those of the above analysis, it will be seen that the magnesium chloride interferes with the solution of both the potassium chloride and with the common salt. Now as the object of clarification is precisely to eliminate this latter, it follows that a potassium salt with low magnesium chloride content, consequently large-grained, will be more easy to purify in this way than a salt with high magnesium chloride content, fine-grained crystals. But clarification is a costly operation because its object is to redissolve a portion of the finished salt, therefore to work economically the original crystallization must be done in such a way as to clarify as little as possible, that is to say, to produce large-grained crystals as far as possible. Starting from the salt analysed above (Table CI) an 80 per cent product would be obtained by a single clarification, whilst a fine-grained salt often requires two, sometimes three, clarifications to get a product of the same strength. It is clear that by this operation products containing 95 per cent or even more may be obtained.

Treatment of the Mother Liquor from the Potassium Chloride.—The mother liquor not used for dissolving is concentrated by evapora-

tion, for it still contains an important amount of potassium chloride. It has a density of about 32° B., and contains :—

TABLE CIII.—ANALYSIS OF MOTHER LIQUOR FROM POTASSIUM CHLORIDE.

	Per cent.
Magnesium sulphate	2·3 to 2·6
" chloride	19·5 to 20·9
Potassium "	5·1 to 6
Common salt	2 to 3

In the evaporation the greater part of the common salt separates out, because it is less soluble when hot than when cold, at the same time as the double salt of potassium and magnesium (schoenite), which is only slightly soluble. This mixture of residual salts often contains 7·5 per cent of potassium, which corresponds to 12 per cent of potassium chloride, or to 14 per cent of potassium sulphate. It is utilized either by extracting the common salt from it or by converting it into manure of low strength. In rational manufacture the residual salt should be washed in the pan itself; for this purpose the mother liquor II is used, as the salt as well as the pan itself is still very hot. When the evaporated solution is run off, the mother liquor with which the pan is drenched heats rapidly and then dissolves the greater part of the potassium salt which is still contained therein. This solution is facilitated by stirring. When the density of the solution determined whilst boiling reaches 34·5° to 35° B., it is run through wrought-iron gutters into special crystallizers, where it deposits not potassium chloride, but a salt with tetrahedral crystals, the composition of which is analogous to carnallite. If the solution was sufficiently concentrated, the liquid which flows from the carnallite crystals (final liquid) only contains 1 to 1·5 per cent of potassium chloride, and in addition :—

	Per cent.
Magnesium chloride	26 to 28
" sulphate	4
Common salt	2 to 4

In certain factories the bromine is extracted, in others the magnesia. The artificial carnallite thus obtained is dissolved in water in smaller pans than those used to dissolve the crude salt. The solution testing 32° to 33° B. is run into vats, where it deposits potassium chloride purer than that produced from the crude salt. The mother liquor of this salt is added to the first. As the carnallite from whence it comes contains less common salt than the crude salt, this mother liquor yields little residual salt. The salt yielded by artificial carnallite is washed with a very little water, and then yields very high strength potassium chloride (95 to 98 per cent).

Drying the Chloride of Potassium.—In most factories potassium chloride is dried in reverberatory furnaces. In recently erected factories the drying is conducted in cylindrical tanks heated by steam coils in which an agitator with blades revolves, and a roller compressor. When the shaft revolves the blades turn up the salt, and the roller which follows makes them into a cake again, so that the surfaces are continually renewed. When the drying is finished the salt is run out through a shoot and bagged up. In a general way factories running on the lines described above are content with producing 80 per cent potassium chloride; rarely carrying the purification so far as to make 97 to 98 per cent products, although the potassium chlorides dissolved by the clarification can be recovered immediately in the crystallizers, whilst the mother liquor is used to dissolve the crude salt. To obtain 98 per cent salt in a simple manner, the method of dissolving the raw salt is modified. The mother liquor, the small amount of clarifying liquor, and finally the liquor used to boil the residual salt, are alone used as solvent, addition of water being avoided. After having brought the solvent solution in the pan to the boil, the raw salt is run in as before and the whole boiled without interruption until the solution tests 35° to 36° B. At that density the carnallite in the crude salt easily dissolves if the liquid be hot enough, i.e. if the steam be of sufficient pressure. Certain factories insert an agitator the action of which contributes to mix the solution, consequently to obtain a better result from the crude salt. Nevertheless, the residue is sometimes still rich in potassium chloride, and if this be the case it is boiled a second time with pure mother liquor. The solution so obtained is clarified in the same way as in the first method; on cooling it deposits not potassium chloride but carnallite, which is allowed to drain, after which it is dissolved in boiling water to extract the potassium chloride. As common salt as well as kieserite only dissolves slightly when hot in a concentrated solution of magnesium chloride, whilst potassium chloride is very soluble therein, it is clear that the solution prepared by this process should contain very little common salt, and also that the carnallite which crystallizes therein should contain very little, and the chloride of potassium furnished by the latter should be of high strength. This method, however, has the drawback of yielding a large amount of carnallite, the removal and solution of which require much labour and steam and consequently fuel. This drawback is obviated by diluting the solution which flows from the clarification vats with water, so that after complete cooling it yields chloride of potassium of high strength directly, and no longer carnallite. In this way the crystallization and solution of carnallite are conducted in a single operation. The advantages of this method of working are evident. Instead of treating as before two different solutions and two different salts, only a

single solution and a single salt have now to be treated. The potassium chloride so produced is so pure that when it is freed from magnesium chloride by a little water it contains only 0·5 per cent of common salt, the remainder being potassium chloride with a little moisture and some slight impurities.

Potassium Sulphate.—This salt is manufactured at Stassfurt, by drenching potassium chloride with sulphuric acid and calcining in a reverberatory furnace. The reaction which takes place is the same as that used in the manufacture of sodium sulphate from common salt and sulphuric acid. First of all the material heats, gaseous hydrochloric acid is given off, and acid potassium sulphate is formed according to the equation—

$$KCl + H_2SO_4 = HKSO_4 + HCl$$

Afterwards, the temperature continuing to rise, the acid sulphate of potassium acts on the remainder of the potassium chloride. A new disengagement of hydrochloric acid gas is produced, and finally potassium sulphate is left as a solid mass. This reaction is expressed by the equation—

$$KCl + HKSO_4 = K_2SO_4 + HCl$$

Since the potassium sulphate as it comes from the furnace is in big lumps, it must be crushed before delivery to farmers. In the same way as the price of potassium chloride is calculated on the basis of an 80 per cent salt, that of potassium sulphate is based on a 90 per cent salt, consequently 100 lb. of this product at 95 per cent equal 110 lb. at 90 per cent. Potassium sulphate of 96 per cent strength is worth about 2½d. more per cwt. on the 90 per cent basis than the product which only tests 90 per cent.

Double Sulphate of Potassium and Magnesium.—This product has already been mentioned as *schoenite*, but is never found in that form; it is manufactured in large quantities from kainit. It consists of equivalent quantities of potassium sulphate and of magnesium sulphate, and contains in the crystalline state six equivalents of water. The method of manufacture varies with the factories, but all processes are based on the lixiviation of the magnesium chloride and common salt from the kainit by hot saline solutions. The dried ground salt contains about 48 per cent of potassium sulphate, corresponding to about 26 per cent of potassium, and it is put on the market with the guarantee of a maximum content of 2·5 per cent of chlorine. This salt is much used as a manure.

It possesses the following composition, according to Mercker :—

TABLE CIV.—ANALYSIS OF SCHOENITE. (MERCKER.)

	Per cent.
Potassium sulphate	50·?
Magnesium ,,	34·0
Common salt	2·5
Water	11·6

Its potassium content is therefore 27·2.

Double Carbonate of Potassium and Magnesium.—The salt contains 17 to 18 per cent of potassium; it consists chiefly, as its name indicates, of the carbonates of potassium and magnesium with 2 to 3 per cent of impurities consisting of potassium chloride and potassium sulphate. This salt, therefore, contains very little chlorine and might perhaps be used as a fertilizer for tobacco. But the price of potassium is about double in this form to what it is in potassium sulphate.

Potash not only acts as a manure but it retains the moisture in the soil. Certain potash salts absorb moisture and cake together; kainit especially forms very hard blocks like stone. Spread in a thin layer it absorbs 2 per cent of moisture in twenty-four hours.

Calcined potash salts absorb from dry air in twenty-four hours up to 6 per cent of water, in five days 14 per cent, and up to 24 per cent in six days. To prevent them caking into a solid mass it suffices to add 2·5 per cent of peat powder; the mixture so prepared keeps for two months without deterioration.

Other Fertilizing Salts.—The Stassfurt factories sometimes make a fertilizer from waste not otherwise utilized. For this purpose the sludge deposited at the bottom of the clarification pans, which always contains a little potash, is used. 100 parts of calcined ground sludge contain:—

TABLE CV.—ANALYSIS OF SLUDGE FROM CLARIFICATION OF POTASH SALTS.

		Equal to potassium.
Insoluble (oxide of iron, sand, gypsum)	6·34	
Calcium sulphate	8·67	
Double sulphate of potassium and magnesium ($MgSO_4 + K_2SO_4$)	16·46	5·27
Potassium chloride	11·01	6·95
Magnesium chloride	10·24	
Common salt	45·51	
Water and loss	1·77	
	100·00	12·22[1]

Another product of this kind is furnished by the residual salt, which contains about 12 per cent of potassium sulphate; as we have seen, this consists of sludge with a large proportion of common salt.

[1] Equal to 19·35 KCl or 22·54 sulphate of potash.

A third salt likewise used as a fertilizer is that extracted from the gutters, which when dry contains about 50 per cent of potassium chloride, and 45 to 50 per cent of common salt.

All these salts are treated in the same way. They are dried in a reverberatory furnace by heating them to nearly the point of fusion, then they are crushed. Brown fertilizing salts with low potassium content are rarely met with now on the market. The salt from the gutters, dried and ground, is sold under the name of "manure salt, calcined and ground," with a minimum guarantee of 27 per cent of potassium. Lately a whole series of other potassic manures has been manufactured, but their high price is an obstacle to their sale. The composition of the different Stassfurt salts are summarized in the table on opposite page.

Commercial Brands of Potassium Chloride (Muriate of Potash).—The principal commercial brands of potassium chloride supplied by the Stassfurt factories are the following:—

(*a*) 70 to 75 per cent potassium chloride (muriate of potash), containing on an average 45 per cent of potash (K_2O) and 21 per cent of sodium chloride, 2·5 per cent of water, 1·7 per cent of sulphate of potash, 0·8 per cent of sulphate of magnesia.

(*b*) 80 to 85 per cent potassium chloride (muriate of potash), containing on an average 50 per cent of potash (K_2O), 14 per cent of sodium chloride and 1·1 of water, etc.

(*c*) 90 to 95 per cent potassium chloride (muriate of potash), containing 56·9 per cent of potash (K_2O), 7 per cent of sodium chloride and 0·6 per cent of water.

(*d*) 97 to 98 per cent of potassium chloride. It is the most concentrated product. For this latter certain factories guarantee not more than 0·5 per cent of sodium chloride, for which an extra charge is made.

The selling price for all sorts is based on 100 kg. (220 lb.) at 80 per cent, bags included, that is to say that products with a plus value are brought to 80 per cent by calculation. An example will make this custom clear. Suppose that the price of potassium chloride of 80 per cent be 9·40 francs, bags included, say 3s. 9d. the cwt. If the muriate bought is of a higher strength (say 95 per cent) it will cost 11·12 francs (say 4s. 6d. the cwt.), that is to say, 100 kg. (220 lb.) of muriate at 95 per cent strength correspond to 118·75 kg. (261·25 lb.) of 80 per cent muriate. It is clear that the price increases proportionately with the purity of the muriate.

As to sulphate of potash the price is calculated on a 90 per cent basis. Consequently 100 kg. (220 lb.) of this product at 95 per cent equal 110 kg. (242 lb.) at 90 per cent. Sulphate of potash of a guaranteed strength of 96 per cent is worth about 0·50 francs (4·8d.) more per 110 kg. (220 lb.), or 2½d. more per cwt., than the sulphate, which only tests 90 per cent.

TABLE CVI.—COMPOSITION OF STASSFURT POTASH SALTS.[1]

Name of the Salts present in 100 parts.	Sulphate of Potash, K_2SO_4.	Potassium Chloride, KCl.	Magnesium Sulphate, $MgSO_4$.	Magnesium Chloride, $MgCl_2$.	Sodium Chloride, NaCl.	Calcium Sulphate, $CaSO_4$.	Insoluble in Water.	Water.	Potash Content. Average.	Potash Content. Guaranteed.
A. Crude Salts. (Natural products from the mines.)										
Kainit	21·3	2·0	14·5	12·4	31·6	1·7	0·8	12·7	12·8	12·4
Carnallite	—	15·5	12·1	21·5	22·4	1·9	0·5	26·1	9·8	9·0
Sylvinite	1·5	26·3	2·4	2·6	56·7	2·8	3·2	4·5	17·4	12·4
Bergkieserite (on demand the crude salts are delivered mixed with peat powder).	—	11·8	21·5	17·2	26·7	0·8	1·3	20·7	7·5	—
B. Concentrated Salts. (Manufactured products.)										
Potassium sulphate, 96 per cent	97·2	0·3	0·7	0·4	0·2	0·3	0·2	0·7	52·7	51·8
Potassium sulphate, 90 ,,	90·6	1·6	2·7	1·0	1·2	0·4	0·3	2·2	49·9	48·6
Double phosphate of potash and magnesia	50·4	—	34·0	—	2·5	0·9	0·6	11·6	27·2	25·9
Potassium chloride, 90-95 per cent	—	91·7	0·2	0·2	7·1	—	0·2	0·6	57·9	56·8
Potassium chloride, 80-85 ,,	—	83·5	0·4	0·3	14·5	—	0·2	1·1	52·7	50·5
Potassium chloride, 70-75 ,,	1·7	72·5	0·8	0·6	21·2	0·2	0·5	2·5	46·6	44·1
Potassium salt for manure, minimum 20 per cent potash	2·0	31·6	10·6	5·3	40·2	2·1	4·0	4·2	21·0	20·0
Potassium salt for manure, minimum 30 per cent potash	1·2	47·6	9·4	4·8	26·2	2·2	3·5	5·1	30·6	30·0
Potassium salt for manure, minimum 40 per cent potash	1·9	62·5	4·2	2·1	20·2	2·4	3·1	3·6	40·4	40·0
Silicate of potash (martellina)	—	—	—	—	—	—	—	—	22·3	—

[1] Averages of numerous analyses by the Potash Syndicate.

Remarks on the Use of Potash Salts as Fertilizers.—As already seen, the Stassfurt mines furnish crude salts and refined salts as fertilizers. Which should preferably be used? This question is of great practical importance, and farmers have very little doubt on the matter, if we are to believe the emphatic puffs of kainit dealers and the other societies "for the encouragement" (so-called) of the diffusion of manures. In the last thirty years the consumption of potassic manures has progressed considerably, but instead of using pure salts the farmer has chiefly used the crude salts, kainit and carnallite. As will be seen in the analyses given below, crude potash salts contain, besides potash, sodium chloride, magnesium chloride, etc.; in fact, they contain much more chlorine than potash.

The following, according to analyses now old, are the potash and chlorine content of crude Stassfurt salts :—

TABLE CVII.—CHLORINE CONTENT OF CRUDE POTASH SALTS.

	Percentage of		Parts of Chlorine per 100 parts of Potash.
	Potash, K_2O.	Chlorine.	
Kieserite	7·44	34·67	466
Carnallite	9·78	37·03	378·6
Ordinary fertilizing salts	12·22	30·53	250
Kainit	12·76	31·21	244·5
Sylvinite	23·04	44·39	192·7
Fertilizing salt, good quality	31·55	52·33	165·9
Muriate of potash, 80 per cent.	52·05	48·68	93·5
" " " 90 "	58·37	47·67	81·6
" " " 98 "	61·48	46·95	75·9
Double sulphate of potassium and magnesium	27·22	1·52	5·5
Potassium sulphate, 90 per cent	49·93	2·23	4·5
" " 96 "	52·68	0·56	1·0
Carbonate of magnesium and potassium	17·18	?	?

More recent analyses of kainit in the agricultural experiment stations have shown that over a long period the proportion of chlorine has been continually increasing.

Thus, in 1895, B. Sjollemay found 35·8 of chlorine. In 1896, Adolphe Mayer found still higher figures. In 1908, chlorine and potash were estimated in fifty-nine samples. A single sample alone gave the same chlorine content as formerly, while the others were as follows :—

	Per Cent.
5 samples	30 to 35
18 ,,	35 to 40
24 ,,	40 to 45
9 ,,	45 to 50
2 ,,	over 50

It is, therefore, established that kainit has not the same composition as formerly. It would appear to be mixed with minerals rich in potash and with a high chlorine content. A more complete analysis of kainit showed that some samples contained only 1·50 per cent of sulphuric acid. Potassium chloride (muriate of potash) contains 50 per cent of potash and 50 per cent of chlorine. In a number of samples of kainit the chlorine content was also 50 per cent, but the potash content was only one-fourth of the amount contained in potassium chloride. This being the case it would be necessary to use four times as much of a manure of this kind to obtain the same result as with muriate of potash. But the high percentage of chlorine in crude potash salts has other drawbacks, not minimized by the fact that it has been forgotten to point them out. Chlorine exerts a disastrous influence on the physical constitution of the soil and on vegetation. Moreover, it cannot be denied that the secondary salts which accompany the potash strongly attack the reserves of fertilizing ingredients in the soil. The potash is evidently absorbed by the soil, if it be supplied to it as chloride or as sulphate of potassium; the potash combines with the silica of the silicates of lime, soda, and magnesia, whilst the secondary elements, such as the chlorine in muriate of potash and sulphuric acid in sulphate of potash, combine with lime, soda, and magnesia. In the first place, calcium chloride is formed, in the second, calcium sulphate. But as calcium chloride is very soluble in water, it is carried by it down into the depths of the soil, and is thus lost to the crop. This fact agrees perfectly with another fact which has been established, viz. that potassic manures, especially the chlorinated manures, rob the soil of its lime; thus 100 kg. (220 lb.) of kainit, containing 31 kg. (78·2 lb.) of chlorine, cause the soil to lose 100 kg. (220 lb.) of lime. It follows, therefore, that the use of potassic manures entails also the use of calcareous manures. Mercker advises to apply to the soil as much quick-lime as potash salts. It thus follows that the comparative cheapness of crude potash salts, such as kainit and sylvinite, is nothing but a snare, because, to take everything into account, the price of these salts ought to be increased by the price of the lime, the loss of which they entail. In marshy land the simultaneous application of lime is particularly necessary. In such soils, in fact, the potash salts are rapidly robbed of their acid in such a way that in the absence of lime the chlorine forms free hydrochloric acid, which

poisons the plant. Lime, moreover, is an indispensable corrective to the secondary effects which crude potash salts never fail to produce, the most important of which is the prevention of nitrification in the soil. Holdefleiss, in experiments with farmyard dung, completely suppressed its action by means of potash salts. The solvent action exerted by the secondary salts of potassic manures is very well brought out in Lawes and Gilbert's experiments. They even obtained an increased yield with salts free from potash. The plots experimented on received every year from 1854, 4 kg. of sulphate of ammonia and 350 kg. of superphosphate. The following amount of salts were added per hectare:—

TABLE CXIII.—EFFECT OF SOLUBLE MINERAL SALTS ON GRAIN CROPS.

	Weight of Crops in Kilogrammes per Hectare.					
	1852-70.		1870-89.		1896.	
	Grain.	Straw.	Grain.	Straw.	Grain.	Straw.
No salt	1868	3404	1417	2543	2036	3737
400 kg. sulphate of potash .	2295	4114	1789	3190	2500	4585
,, ,, ,, ,, soda .	2275	4240	1883	4674	2775	5602
,, ,, ,, ,, magnesia	2289	4051	1882	3291	2369	4333

It will be seen from these figures that salts free from potash have in several cases furnished yields heavier than with the pure potash salt. These salts, therefore, have mobilized the reserves of fertilizing ingredients in the soil, so as to bring them to the support of the plant. The soil has thus been, in a way, robbed of its normal reserve in favour of a few crops. This robbing of the soil would have been demonstrated in a more serious manner if the investigators, instead of using sulphates, had used chlorides, because then it would have been intensified by loss of lime. In fact, although not stated, here again the nutritive substances of plants, including phosphoric acid, may be rendered soluble and consequently carried down into the depths of the soil. The same phenomena must perforce occur with kainit, sylvinite and carnallite, the comparative low proportion of pure potash salts making their action almost nil compared with that of the secondary salts which accompany it in these products. There is here a very interesting subject for study by agronomists. It would be specially useful to find if drainage water contains fertilizing substances in

those cases where crude potash salts are used. Amongst these fertilizing substances, phosphoric acid may be found, for we must not forget that phosphate of lime is soluble in a great number of saline solutions. There might also be found in the drainage water as much potash as was spread on the soil, and if such were the case it would prove that the use of crude potash salts as manure would be absolutely illusory. It is probable that no delay will arise in discontinuing the use of crude potash salts, using only the pure potash salts, in spite of their higher price, when the devastating action of the secondary elements which accompany the potash in the crude salts is realized.[1]

Potash Salts Deposits of Alsace.—Deposits of potash have been discovered in Alsace. They consist chiefly of sylvinite. According to report from the President of the district of Upper Alsace, the deposits of rock salts and of potash occur in the *Tertiary System.* The territory in question extends over an area of about 200 sq. km. (125 square miles). It is bounded on the north by the line Regisheim-Soultz, to the west by the line Soultz Berrweiler-Schweighausen, to the south by the line Schweighausen-Neidermorschweiler-Ile Napoleon, and to the east by the line Ile Napoleon-Ensisheim-Regisheim. The total thickness of the deposit is estimated at 200 metres (656 feet), and the beds of potash salt are included therein, fairly regularly. These deposits appear destined to play a part in the German potash industry.

German Potash Industry.

Quantities of Potash Salts in Double Hundredweights of Potash (K_2O) raised in Germany, with Home Consumption and Values.

	1913.	1914.	1915.	1916.	1917.
Exported	5,055,960	3,684,260	1,191,500	1,570,400	1,305,890
Home consumption . .	6,046,780	5,357,110	5,608,250	7,266,560	8,736,960
Total	11,103,694	9,039,883	6,797,764	8,839,759	10,042,850
Value, Millions of marks .	202½	164½	111¾	164	230

[1] Whilst muriate of potash should be used sparingly and with the greatest discrimination, kainit when fairly free from chlorine is a safe and most valuable manure, especially for potatoes. The translator considers it sound practice to add 1 cwt. to 2 cwts. of such kainit per ton to all compound manures, that is when it can be done without lowering the percentage of the phosphoric acid and nitrogen below the minimum guarantee. Potatoes respond in a very remarkable manner to such a manure.—Tr.

According to the "Chemical Trade Journal" (Jan. 28, 1911), there were at that date 69 works engaged in the production of potash salts, and in several cases purifying or preparing it for market. In addition, there were 79 works in process of construction and 25 more under course of promotion. Twenty-four firms are engaged partially or entirely in the prospecting and boring for potash minerals, so that altogether 197 firms are employed directly in the potash industry.

The number of syndicated works and the total sales and values are given in the following table:—

GERMAN POTASH INDUSTRY.

Total Sales of Potash Salts in Terms of K_2O and Values.

Year.	No. of Syndicated Works.	Total Sales.		Average Sale per Syndicated Work.	
		Quantity (Dop. Zent).	Value (Marks).	Quantity (Dop. Zent).	Value (Marks).
1900	12	2,942,540	56,230,316	245,212	4,685,860
1901	19	3,328,890	59,128,509	175,205	3,112,027
1902	23	3,097,536	56,889,087	134,675	2,473,439
1903	27	3,583,238	64,108,854	130,861	2,374,402
1904	27	4,191,422	74,077,764	129,312	2,743,621
1905	28	4,882,682	81,642,749	172,596	2,915,812
1906	34	5,474,436	91,683,987	161,013	2,696,588
1907	40	5,577,546	93,422,074	139,439	2,335,552
1908	49	5,915,761	97,813,218	120,730	1,966,188
1909	56	6,758,318	116,505,730	120,595	2,080,459
1910[1]	65	8,000,000	123,000,000	123,077	1,892,307

In 1918 Dr. Paul Kestner gave a most important address in London on the Alsace Potash deposits[2] from which the following notes are taken:—

Consumption of Potash Salts.—The amount of potash salts applied to the land in different countries amounted to 1400 kilos per square centimetre in Germany, 183·9 in England, 96 in France and 128·9 in the United States, the total amounts consumed being given in the following table:—

[1] Estimated. [2] "Jour. Soc. Chem. Indt.," 1918, T. p. 291.

Year.	Germany. Kilos.	United States. Kilos.	England. Kilos.	France. Kilos.
1910	359,335	244,910	18,258	22,849
1911	422,340	237,442	20,902	26,468
1912	463,383	215,965	23,414	31,691
1913	536,102	231,689	23,410	33,115

North German Deposits.—About the year 1850 a most important discovery of potash salts was made at a depth of about 260 metres in the rock salt mines at Stassfurt. The value of potash salts in agriculture was not at that time realized, and it was only later that the deposits were worked for its extraction, the rock salt being the object of attention. Soon, however, companies began to be formed for the working of the potash-bearing minerals and these were gradually multiplied until there were quite a large number of workings, not only at Stassfurt but also in other parts of the district comprised in the Duchies of Brunswick, Hanover, Mecklenburg, and Thuringia. The first workings were started in 1862, while by 1907 there were 39 companies engaged in the industry, these being amalgamated into one large syndicate or trust, which was very well known, under the name of the Kali Syndicate, owing to the fact that it held practical control of the world's supply of potash salts and regulated the amount of material to be raised, the amounts to be allocated for home consumption and for export, and the prices to be paid. Owing to its well organized methods of propaganda among the farmers the production of potash salts rose rapidly from year to year, amounting in the aggregate to 11,607,000 tons, half of which was reserved for home consumption. During the war very little was exported.

The composition of the salts given by Dr. Kestner is somewhat different to those already quoted. The most important is sylvinite, a mixed chloride of potassium and sodium, containing 26·3 per cent of potassium chloride, but this is rather scarce in the North German deposits. Kainite is a mixture of potassium chloride and magnesium sulphate containing 26·6 per cent of potassium chloride. "Hartsalz," a mixture of potassium and sodium chloride with magnesium sulphate, contains 21·2 per cent of potassium chloride; carnallite, a double chloride of potassium and magnesium, contains 15·5 per cent of potassium chloride, while polyhalite contains varying proportions of the sulphates of potassium, sodium, and calcium.

The great majority of the salts from the North German deposits contain a high percentage of magnesia, for which reason they require to be refined before they can be used in agriculture. For this purpose huge refining factories have been established by the syn-

dicate ... the preparation of salts containing a fixed proportion of potassium chloride.

Alsatian Deposits.—In 1904 the potash deposits of Alsace were discovered. These contain much richer salts than those of Stassfurt and although companies were formed to work them it was not long before the powerful North German syndicate obtained a controlling influence in these concerns and practically strangled the industry so as to remove any danger from competition, and by this means secured a practical monoply of the world's supplies, which they fondly hoped could be made a very formidable weapon in any trouble with other countries. The Alsace deposits cover an area of about 200 square kilometres (= 78 square miles) in the North-West of Mulhouse, between the Jura to the south, the Vosges to the west and the Rhine on the east. The deposits are found at a depth of 650 to 1000 metres and consist of two beds, the lower one being the most extensive in area and in thickness, averaging 4 metres. The distance between the two beds is 15 to 25 metres, and they are covered with a huge bed of rock salt about 240 metres in thickness. The salts consist mainly of pure sylvinite, the upper bed containing on an average about 35 per cent of potassium chloride and the lower 30 per cent. The total capacity of the two layers is estimated at about 700,980 cubic metres, equivalent to 1,472,058,000 tons, with an average content of 22 per cent of potash (K_2O), or in other words the deposits represent 300,000,000 tons of potash, which is sufficient to supply the world's requirements for a good many years. The purity of the salt far surpasses those of the Stassfurt area and, in fact, is superior to that of any other known deposits of importance. It is, in fact, sufficiently pure to be suitable for use in agriculture without being refined. The first boring undertaken was near Wittelsheim in 1904, coal being the object sought. At a depth of 358 metres beds of rock salt were discovered. The boring was continued to a depth of 1129 metres without any coal being found and the potash deposits were passed through without their presence being observed until later it was discovered in some of the material removed. A company was then formed to exploit this discovery and 165 borings were made in the district. Working in the first shaft was commenced in 1910, and already 15 shafts have been sunk. The powerful German Potash syndicate, fearing the result of competition, obtained a controlling influence in these deposits, and in order to protect their own companies, imposed many restrictions upon the Alsace mines, only 5 per cent of the total potash production in Germany being allowed to be raised therefrom. The remarkable anomaly there exists that, owing to the short-sighted policy of the German magnates, the richest deposits in the world have had to be handed back to France almost untouched.

Galician Deposits.—Deposits of potash have been worked in Galicia for several years, but they do not appear to be of any great importance since they are unable to supply the whole of the requirements of Austria-Hungary, which in 1913 imported 21,000 tons of potash from Germany.

Spanish Deposit.—A deposit of potash salts was discovered just prior to the war at Suria, in Catalonia, where rock salt mines were already being worked. Several borings were made and deposits were located at depths between 121 and 197 feet, others were also found at 420 feet and also at 886 feet—the greatest depth to which the borings were carried; below this again is rock salt. The deposit comes to the surface at Cardona where there is actually an outcrop in several places, and a stream running near the salt mines contains a notable proportion of potash, which has evidently been running to waste for a long time. The deposits seem to be fairly extensive but, owing to the irregular geological formation of the country around Barcelona, the amount of potash salt that can be mined cannot be determined with any accuracy. In the area in which the borings have been made, extending over 2,690,000 square feet, the deposits are 260 feet thick, and contain 70 feet of carnallite with 12 to 20 per cent of potash, and 33 feet of sylvinite containing 9·5 per cent of potash. It is estimated that there is approximately 255,000 tons of carnallite and 1,150,000 tons of sylvite. From a survey of the region it is regarded as probable that further deposits are likely to occur in the neighbourhood of those already discovered. The beds are, however, not continuous, and, unlike those of Alsace, which are nearly horizontal, they are steeply inclined, which adds very materially to the difficulty of working them. The original concession, granted to a Franco-Belgian company at Suria and Cardona is apparently the most valuable, being 10 kilometres in width, 12,000 hectares in extent, and now covered with 12 shafts 300 to 850 metres in depth. A shaft was being sunk which in 1919 would be capable of yielding 1000 tons of salt per day. A concession has also been granted to another company which has already sunk 3 shafts at Cardona.

Italian Deposit.—At Erythrea a layer of potash salts has been discovered in what appears to be the bed of an ancient lake. It is extremely rich in potash salts, containing as much as 80 per cent of potassium chloride. A company are now working the deposit, and it was estimated that the output for 1918 would be 50,000 tons.

Indian Deposits.—Potash deposits have been found in the Mayo salt mine at Kheura, Punjab, the chief minerals being langbeinite ($K_2SO_4,2MgSO_4$), and sylvite. Average samples taken from the Pharwala-Sujowal, Buggy, and Nurpur seams showed respectively

8·0, 11·9 and 11·3 per cent of potash to be present. These deposits have not yet been worked for potash manufacture.[1]

Salt Lakes.—Sea water contains a small quantity of potash salts, and where the heat of the climate is considerable common salt can be obtained by solar evaportion of the water in shallow tanks, or better, by pumping it over brushwood stretched upon a huge frame of wood. After the crystallization of the common salt the mother liquor or "bittern" contains sufficient potassium chloride, bromine, etc., to make it worth while extracting them. At Salin Girand there are 123 acres of earthen lagunes and 40 acres of cemented tanks.[2] The water is concentrated by a combination of Balards' and Merles' processes to a gravity of 35° B. After the separation of Epsom salts, which occurs first, there is a deposition of mixed salts containing magnesium sulphate and common salt. The mother liquor is drained into a large tank in which it is refrigerated, whereupon carnallite ($KCl,MgCl_2 + 6H_2O$) separates out. On washing this with its own weight of cold water most of the magnesium chloride dissolves out, with but little potassium chloride, and the residue then contains 75 per cent of potassium chloride. 75 cubic metres of sea water yield one cubic metre of evaporated brine of 28° B, from which is obtained 10 kilogrammes of potassium chloride. These works have an output of 900 tons potassium chloride per annum.

United States Deposits.—Deposits of potash salts have been found in several of the salt lakes in the United States and are evidently being continuously formed by the solar evaporation of the water. These salt lakes, having practically no outlets, and there being also very little rain in the districts, the water which finds its way into the lakes rapidly evaporates, becoming more and more salty until finally it is saturated, and tne salts crystalize as a crust which forms a solid deposit on the bottom and gradually grows in thickness. No doubt all the salt deposits of the earth have been formed in this way, alternating layers of common salt, magnesium and potassium compounds, gypsum, etc., being found in many of them. Several lakes of this kind are found in the rocky mountains in the States of Nebraska, Utah, and California. At Searles lake in California, the American Trona Company, which is largely a British corporation, are engaged in concentrating the water, and extracting potash salts from it. Considerable reserves of material have been accumulated, and when the projected extensions are completed it is estimated that the daily output of salts will be equivalent to 100 tons of potash. A company is also erecting a plant at Keelar, on the shores of Owen's lake, California.

[1] "Imp. Inst. Bulletin," 1915.

[2] C. G. Cresswell, "Jour. Soc. Chem. Indt.," 1915, p. 388.

Two works are also being started at the Great Salt Lake.[1] In Nebraska several of the more saline sand-hill lakes are being opened out at Hoffland, Antioch, and Lakeside. The brine in these lakes is found below a thin layer of hardpan at the bottom of the lakes. It is pumped to the evaporating plant which consists of evaporating pans and rotary driers. The salt is sold in the crude state, one sample of the material having the following composition: Water 2·14, potash (K_2O) 27·35, soda (Na_2O) 28·39, carbonic acid (CO_2) 22·44, sulphuric acid (SO_3) 16·77, and chlorine 2·02 per cent.[2]

In other cases the brine is evaporated by spraying it into an oil fired furnace, similar to those used in the manufacture of cement, or it is dried to a clinker, which, while still in a highly heated state, is sprayed with the brine, which causes it to fall into a crumbly mass. In the Nebraska region potash salts, containing 25 per cent of potash, are being produced at the rate of 32,000 tons of K_2O per annum. Previous to the war the consumption of potash salts in the United States was 275,000 tons per annum, whereas in 1916 the total home production was only 9720.[3] There are also several solar evaporation plants on San Francisco bay.

Chilian Deposits.—In the province of Tarapaca, there are deposits of potash salts in the lakes Pintados and Belle Vista. These lakes have a total area of about 100,000 acres, and are only three miles from the railway which runs from Iquique to Lagunas. The salts occur in the form of a crust on the surface of the brine and contain from 3 to 36 per cent of potassium chloride. The density of the material is about 1·352 and the average thickness 20 c.m. It is estimated that there is a reserve of 2 million tons of potassium chloride. The brine underlying the crust of salts contains 8 kilos of KCl per cubic metre. After removal of the crust it again forms in 8 to 12 years. Analysis of an average sample of the salts gave the following figures: Potassium chloride 14·15, sodium chloride 51·45, sodium sulphate 29·39, sodium carbonate 0·32, calcium sulphate 0·93 per cent with only a trace of magnesium.[4]

Tunisian Deposit.—In Tunis also there is a salt lake to the south of Gabes, which since 1915 has been worked both for potash and bromine. The brine is evaporated by solar heat. In 1917 20,000 tons of salt was obtained from this source, but this will be increased to about 100,000 tons when the installations in course of completion are working. The salt is known as sebkainite and contains 40 per cent of potassium chloride. Refineries have been installed for the production of pure potassium chloride.

In addition to the sources already mentioned there are deposits

[1] "U.S. Geol. Survey," Apl. 1916.
[2] R. P. Crawford, "Eng. and Min. Jour.," 1917, p. 777.
[3] E. E. Thum, "Met. and Chem. Eng.," 1917, p. 693.
[4] S. Salcedo, "Eng. and Min. Jour.," 1915, p. 218.

in Peru, Russia, Morocco, the Province of Overyssel in Holland, and also in Sicily, none of these, up to the present, having been exploited.

Manufacture of Potash from Felspar and other Potassic Minerals.—The felspar is finely crushed, beaten up with water, then run into a wooden vat placed in a large receiver of any material. The outside receiver is then filled; the inside receiver is then connected with the positive pole and the outside receiver with the negative pole of an electric current. This partially liberates the potash, the soda and the other soluble bases, freeing them from the compounds which they form with silica. The soluble bases traverse the wooden wall of the interior vessel and pass into the water of the exterior vessel which they render alkaline. However, the felspar soon ceases to decompose. To render the decomposition more rapid and more permanent the mass in the interior vessel is continually stirred or hydrofluoric acid added. To obtain nitrates, sulphates, and chlorides, in place of caustic alkali, it suffices to add the corresponding acids to the water in the outside receiver. American patent No. 851,922 of April 30, 1907.

Production of Potash from Mineral Sources.—Several minerals, such as felspar and mica, contain sufficient potash to make it worth while extracting it if only some simple method of treatment could be devised and that a use could be found for the large amount of residual matter which would result from its treatment.

Potash felspar, or orthoclase, contains about 15 per cent of K_2O and potash mica or muscovite 8 to 11 per cent, and many processes have been devised or patented for their treatment.

It would not be possible here to enter very closely into the details of these processes but reference may be made to a monograph on the subject prepared by A. S. Cushman and W. Coggleshall, read before the 8th International Congress of Applied Chemistry.[1] Both Cushman[2] and Coggleshall[3] have taken out patents in America for the extraction of potash from felspar.

In Cushman's process the finely powdered felspar 100 parts is mixed with 20 parts of lime and 10 to 20 parts of common salt. This mixture is fed on to a revolving drum in a thin layer, and is sprayed with a strong solution of calcium chloride, which cements the powder into "clumps". The "clumps" are heated in a rotary kiln with a blast of air and powdered coal. The product contains about 6 per cent of soluble potash and is used direct as a fertilizer, no attempt being made to extract the potash. Another process described by the above authors consists in heating powdered felspar and burnt lime in a rotary kiln, lixiviating the product with water,

[1] "Jour. Ind. Eng. Chem.," 1912, 821.
[2] U.S. Pat. 981,436. [3] *Ibid.*, 987,544.

and evaporating the solution by spraying it into the hot gases and then in a rotary drier. The residue contains 70 to 80 per cent of KCl and 14 to 16 per NaCl, with small amounts of lime and moisture.

Rhodin[1] states that when 40 parts of slaked lime, 40 parts of salt, and 100 parts of powdered felspar are heated to 900° C., 80 to 90 per cent of the potash present is converted into chloride. A sub-committee of the Government's Fertilizers Committee have examined Rhodins' process and were favourably impressed with it, various felspars yielding 54 to 75 of their potash in soluble form.[2] Ward and Wynant,[3] Thompson,[4] Newton,[5] H. Blumenberg,[6] and others, have also taken out patents for the extraction of potash from potash-bearing rocks.

At a meeting of the Institute of Mining and Metallurgy, E. A. Ashcroft gave the details of a process in which the finely-crushed felspar is heated with common salt to a temperature of 900° to 1000° C. out of contact with air and moisture.

$$2NaCl + K_2OAl_2O_3(SiO)_6 = Na_2OAl_2O_3(SiO)_6 + 2KCl$$

The products are potassium chloride and soda felspar. The latter being insoluble in water the potassium chloride can be leached out; it contains some sodium chloride. With a felspar containing 8 per cent of K_2O, 87 per cent of it could be extracted. The author mentions that although E. Bassett took out a patent in 1913 for this process it was never successful, because he did not realize that in order to get efficient results moisture and air must be excluded.

Manufacture of Potash from Alunite.—Alunite is a hydrated double sulphate of aluminium and potassium, $KAl_3(SO_4)_2OH)_6$. It occurs in the form of a mineral in volcanic districts. In the Lipari Islands, Auvergne, and the Isle of Milo, in Europe, and near Mary's Vale, Utah, in the United States. The latter deposit occurs in the form of a large vein 6 to 20 ft. thick, penetrating the volcanic rock at a steep inclination. The mineral contains 9·7 to 10·5 per cent of potash. Taking the average thickness of this deposit as 10 ft. over a length of 3500 ft., the outcrop has a surface area of 35,000 sq. ft. and it is calculated that the total amounts to at least 300,000 short tons, equal to 30,000 tons of potash.[7]

A similar mineral to the above, known as "Galafalite," has been found near Benahabux, 6 miles from Almeria, Spain, and concessions have been granted over 2470 acres.

On ignition alunite decomposes, forming potassium sulphate,

[1] Eng. Pat. 1899, 16,780.
[2] "Jour. Board Agric.," 1917, 1087.
[3] Eng. Pat. 1857, 3185.
[4] U.S. Pat. 1911, 995,105.
[5] Eng. Pats. 1854, 1211 and 2421.
[6] U.S. Pat. 1917, 1,214,003.
[7] "U.S. Geol. Survey, Bull." 511.

and alumina, which latter is insoluble in water. In this state it can be used as a fertilizer or can be treated for the extraction of the potash salt. Sulphate of potash prepared from alunite was placed on the market in the United States by a company working the Mary's Vale deposit.

Potash from Blast Furnace Gases.—In 1884 a patent was granted to Hugh Barclay and Robert Simpson of the Harrington iron works, Cumberland, for the recovery of salts, especially those of potash from coke-fed furnaces.[1]

In 1914 a Halberg-Beth plant for the separation of the dust from blast furnace gases, installed by Fraser and Chalmers, Ltd., at the works of the North Lincolnshire Iron Co., Ltd., was brought into operation. On investigation it was found that this dust contained a large quantity of potash and cyanides which had been volatilized from the charge. Owing to the shortage of potash salts it was felt that this discovery was of the utmost importance, and arrangements were entered into with the British Cyanides Co. Ltd., to carry out investigations with a view to the manufacture of potash salts from this dust.[2]

A sample of the dust gave the following figures on analysis: *Soluble in water*—potassium cyanide 5·58, potassium carbonate 14·66, potassium bicarbonate 23·23, potassium sulphocyanide, trace, potassium sulphate 1·13, potassium chloride 10·90, sodium carbonate 3·97 per cent, ferrous cyanide 0·48, zinc and lead as sulphides 0·36 per cent. *Soluble in hydrochloric acid*—magnetic oxide of iron 11·68, zinc sulphide 2·23, calcium carbonate 10·39, magnesia 1·05, also silica 8·91, and carbon 2·18 per cent.

It was found that the whole of the potash in the charge was not volatilized under the conditions prevailing in the furnace, and experiments made with a view to increasing the yield met with very considerable success. Thus it was found that by increasing the amount of lime in the charge and at the same time raising the heat the amount of potash as carbonate in the flue dust increased from 40 lb. of alkali per million cubic feet of gas to over 100 lb. and even as much as 140 lb. It was also discovered that common salt had an even more beneficial effect, the chlorides in the gas increasing from about 30 lb. to 200 lb. per million cubic feet, the ratio of soda to potash, i.e. 1 to 9, was not affected, and the total potash was thus raised from about 60 lb. to 200 lb. per million cubic feet. A patent was taken out for this process[3] which works quite satisfactorily and gives no trouble whatever. The extra cost entailed in this process is that due to the salt, i.e. £1 per ton of salt or 15s. per ton of

[1] R. A. Berry and D. N. McArthur, "Jour. Soc. Chem. Indt." 1918, 1 T.

[2] Kenneth M. Chance, "Jour. Soc. Chem. Indt.," 1918, 222 T.

[3] British Cyanides Co. Ltd., K. M. Chance, E. Rossiter, and the North Lincolnshire Iron Co. Ltd., Eng. Pat. 112,338, 1917.

potash and carriage of the dust to a central factory for treatment, say 5s. per ton of dust or 12s. per ton of potash. The cost of the potash in the raw material would thus not exceed 27s. to 30s. per ton, and potash salts could be extracted from it at a much less cost than has ever been charged for German potassium chloride delivered in this country (£8 per ton) after providing a sufficient profit for the blast furnace owner and the refiner. In a further paper on the subject, the above-mentioned author states that the burden of materials normally charged into a blast furnace to produce 1000 tons of pig iron will contain 15 to 30 tons of potash (K_2O). This being the case the amount of potash annually fed into the blast furnaces of this country amounts to at least 200,000 tons, 50,000 tons of which is carried off in the blast furnace gases. This can be very considerably increased, as above described, and the greater part of the potash in the gases can be recovered from the dust. It is possible by very simple means to obtain a potash fertilizer of 95 per cent purity, whereas German kainite contained only 20 per cent of potash.

R. J. Wysor[1] examined the yellowish dust which deposits at the base of the stone checquer work in the stoves and gas-fired boilers, and found that it contained 15 per cent of potash. In 1916 an experimental Cottrell electric plant for precipitating the dust was installed. This was connected to the gas main, leaving one of the dust catchers, and it was soon demonstrated that the whole of the dust could be successfully extracted. The dust varied in colour from light to dark grey and contained on an average 10 per cent of potash. The total quantity of potash charged in per ton of pig iron produced amounted to 22·4 lb. of K_2O. The amount passing out in the slag is 20 per cent of the whole (that is 2·2 lb.) which, together with that deposited in the dust catcher, gives a total of 6 lb., so that at least 15 lb. of potash per ton of iron could thus be recovered. The production of pig iron in the United States in 1916 amounted to 15,000,000 tons, so that the potash which could be extracted from coke-fed furnaces amounts to a very respectable figure. As an example of what could be done even before the Cottrell plant was installed, Wysor states that at the Bethlehem Steel Company's Works during the period 1 April, 1915 and 1 July, 1916, 36 car loads of dust were collected, weighing altogether 1073 tons, and from this 106 tons of water-soluble potash was obtained. This, however, represents only a portion of what it is possible to obtain with the electrical precipitation process.

In countries such as Scotland, where the blast furnaces are fed with coal instead of coke, much tarry matter is precipitated with

[1] R. J. Wysor, "Metall. Chem. Eng.," 1917, p. 205.

the dust, at the same time there is less potash contained in the ores and the amount volatilized is not so great.[1]

The amount of potash contained in iron ores varies very considerably, as shown by the figures obtained by E. F. Burchardt,[2] viz. from 0·70 to 2·56 per cent, and by Grasby,[3] who found 0·70 to 2·29 with an average of 1·32 per cent. H. T. Cranfield[4] has made a very close investigation into the composition of the dust which is deposited from blast furnaces. From one furnace in the course of a week 20 tons of dust, containing 2·5 per cent of potash, was deposited in the dust catcher, 5 tons of reddish dust (K_2O, 7·0 per cent) in the stoves and boilers, and 1 ton of cream coloured dust (K_2O, 10 per cent) at the base of the chimney stacks. He estimates that the amount of potash available in Great Britain from this source amounts to 15,000 tons, but this is assuming that the Scottish furnaces produce as much dust as the English, which is not the case.[5] R. A. Berry and D. N McArthur examined a number of deposits from different works and found in flue dusts 3·13 to 19·49 per cent of water-soluble potash, stove dusts 6·86 to 7·87 per cent, tube cleanings (which are produced in large quantity) 0·3 to 2·7 per cent. The spent liquor from the scrubbing apparatus contained 0·321 to 156·58 grms. of potash (K_2O) per gallon, and this on evaporation and ignition yielded an ash containing 20 to 55 per cent of water-soluble potash. The pitch contained 17 per cent of ash, and in the ash there was 8·8 per cent of water-soluble potash, while the slag contained 0·24 per cent of potash.

In one works the raw materials contained the following percentages of potash :—

	Per cent.
Spent coal	0·040
Coke	0·121
Iron ore	0·128
Limestone	0·136

From these figures it is calculated that the amount of potash in the raw material charged into the furnaces amounted to 7·6 lb. per ton of pig iron produced, and the quantities found were as follows :—

In spent liquor	1·4 lb. per ton.
In flue and stove dust	0·04 „ „ „
In pitch	1·7 „ „ „
In tube cleaning	0·2 „ „ „
In slag	2·7 „ „ „
	6·04
Unaccounted for	1·6

[1] "Chem. Eng. Manuf.," 1917, 24, No. 5.
[2] *Ibid.*, 1917, 24, No. 3. [3] *Ibid.*, 1916, 124.
[4] "Jour. Board of Agric.," 1917, 526.
[5] R. A. Berry and D. N. McArthur, "Jour. Soc. Chem. Indt.," 1918, 1 T.

Mr. F. G. Kelloway, Parliamentary and Financial Secretary to the Ministry of Munitions, in a speech made in 1918, stated that the design of the German Halberg-Beth plant had been modified so as to obtain greater reliability and lower capital cost, also that an entirely new method of recovering potash from blast furnace gases had been devised, and two large plants of this type were in course of erection capable of producing 1600 tons per annum. Altogether plants in work and in course of erection in this country would be capable of recovering about 18,000 tons of potash per annum.

Potash from Cement Kilns.—It has been known for several years that the dust from cement kilns contained an appreciable proportion of potash, and during the last few years the recovery of the potash thus volatilized has become an accomplished fact. Analyses of the raw materials and cement clinker from 113 works in America have been made by W. H. Ross and A. R. Merz.[1] The raw materials contained from 0·2 to 1·16 per cent of potash (K_2O) and it is estimated that the potash volatilized per barrel of cement made at different works amounted to between 0·35 and 5·34 lb. Leaving out of account those works using blast furnace slag the amount of potash volatilized averaged 2·09 lb., which for the whole of the United States would represent about 87,000 tons per annum. By using the Cottrell electrical plant for precipitating the dust 99 per cent of such dust can be precipitated, but as the lighter dust is relatively much richer in potash it is safer to place the potash recovery figure at 90 per cent, which would give 78,000 tons altogether. This applies only to gas-fired kilns; with coal-fired kilns the proportion of potash in the dust is much lower, that is, only 59·6 per cent as against 91·6 per cent actually obtained with an oil-fired kiln. The potash content of the dust can be increased by the addition of potash-bearing minerals to the charge, also by adding common salt or calcium fluoride which form volatile chloride or fluoride. The same result can also be attained by increasing the heat of the furnace.

According to a report of the U.S. Geological Survey, published in April, 1916, potash was produced on a commercial scale in 1915 from cement kilns at Riverside, California, and not only is this saving effected, but the dust, which was estimated to amount to 100 tons per day, is recovered and added to the cement making materials, and not as heretofore being discharged over the surrounding orange groves.

J. G. Dean states that at the works of the South-western Portland Cement Company, Victorville, California, one ton of potassium sulphate is recovered per day from the cement kiln dust, which is extracted by saturating the kiln gases with moisture and then cooling

[1] W. H. Ross and A. R. Merz. "Jour. Ind. and Eng. Chem.," 1917, p. 1035.

them as much as possible prior to their discharge. In this way the dust is thrown down in the form of sludge which contains potassium sulphate, sodium sulphate, and the sulphides, polysulphides, and thiosulphates of these metals. The soluble salts are leached out with water, and the solution evaporated when potassium sulphate and a hydrous double thiosulphate of potassium and sodium crystallize out. This is dried and calcined, yielding a product containing 90 per cent of potassium sulphate. The kilns are oil fired, and owing to the comparatively low temperature in the kiln, due to the reducing conditions of the flame, only about 45 per cent of the total potash in the raw materials is volatilized. More potash could be volatilized with an oxidizing flame, but under these conditions it was found that the difficulties encountered rendered the process unworkable.

The Cottrell plant installed at the Hagerstown works of the Security Cement and Lime Company in 1916 precipitates the dust by means of a high-tension current at 70,000 volts. The power supply consists of a three-phase current at 440 volts and 60 cycles, the electrical equipment consisting of four 15 H.P., 10 k.v.a., 220 volt single phase 60 cycle, 1800 r.p.m. motor generator sets, each of which is connected to the shaft of a rotary rectifier, and four 220 to 70,000 volt, 60 cycle, 10 k.v.a. transformers of special design. The volume of flue gases dealt with is about 180,000 cb. ft. per minute, and from five kilns 7-8 ft. by 100-125 ft. the yield of dust amounts to 20 to 25 tons per day. The dust is extremely fine and contains 5 to 10 per cent of potash (K_2O) combined as sulphate.[1]

Manufacture of Potash in the Caucasus.—The manufacture of potash is an accessory industry of the cultivation of sunflower, the ashes of the stem and the branches of sunflower yielding the raw material. The first potash factory was established in 1899 at Maikopp, by Schaponalow. Difficulties occurred at first owing to the want of experience. But gradually the conditions of production improved, and fresh factories were started. The official statistics in 1906 state that eleven factories produced 475,563 poods of potash. According to information supplied by the manufacturers twenty-four factories were at work in 1907, some of them producing several thousands up to as much as 200,000 poods of potash. The total production of these factories being from 700,000 to 900,000 poods, representing a value of 22,000,000 roubles. The stems of the sunflower are generally burnt by the farmers themselves. But certain manufacturers also burn the plant and buy the stems of 10,000 to 15,000 deciatines, for which they pay 3 to 4 roubles per deciatine. A deciatine of sunflower yields in good ground 200 to 300 poods of stems and in bad ground 100 poods only, from

[1] "Jour. Soc. Chem. Indt.," 1916, p. 827.

which 3 to 5 per cent of ashes may be extracted, and 3 to 4 poods of ashes give one pood of potash. The percentage of carbonate of potash is 20 to 35 per cent. The appearance of the ash is improved by throwing it into the fire, for instance, which causes the ash to fuse and gives it a vitreous appearance.

When the sunflower harvest is finished the stems are burnt. The purchase of ashes is finished in September, whilst the manufacture of potash lasts five to six months. The price of the ashes up to recently has been 35 copecks, but owing to competition it has risen to 40 and 60 copecks per pood. The manufacture of potash is conducted in a very primitive fashion, which consists in lixiviating the ashes, methodically concentrating the lyes, and calcining the product. The product is packed in casks of 30 to 40 poods. The analysis of a potash from Kuban gave (per cent) water, 1·74; carbonate of potash, 89; carbonate of soda, 5·0; sulphate of potash, 2·01; potassium chloride, 6·51; insoluble, etc., by difference, 0·74; the usual potassium carbonate content is 90 to 91. It is dealt with on a basis of 90 per cent with 2 per cent margin at least. Three-fourths of the potash is exported to Hamburg, London and New York.

Potash salts have been from the very earliest time made from wood ashes. These were lixiviated with water and the solution evaporated, yielding "pot-ashes," an impure form of carbonate of potash. By again lixiviating with a little water and evaporating and drying, a purer form of carbonate was obtained known as "pearlash". This industry was practically killed on the introduction of the Stassfurt salts, but in the north-west of the United States and in Canada, where wood is very plentiful, there is still a small but dwindling industry, the production in Canada in 1894 being 1936 barrels, and in 1898, 1080 barrels. Suggestions have been put forward from time to time for the utilization of waste vegetable matter as a source of potash. Thus in 1802 Hudson [1] took out a patent for the production of potash from tanner's bark, bean and other straw, fern, furze, broom, and kelp. J. C. Umney [2] proposed the systematic collection and incineration of furze, bracken, hedge clippings, etc., and gives the following figures for the potash content in the ash: bracken 60, *Boletus edulis* 50 to 57, *Agaricus velutipes* 78, *Hypnum Schroberi* 28 to 30, groundsel 43·5, broom 33, and *Euphorbia amygdaloides* 39 per cent. According to Quaintenne,[3] mangrove trees growing in fresh water absorb a large proportion of potash.

H. Bradley [4] published an account of the method of extracting

[1] Eng. Pat. 2586, 1802.
[2] J. C. Umney, "Jour. Soc. Chem. Indt.," 1914, p. 1046.
[3] "Jour. Soc. Chem. Indt.," 1905, p. 1302.
[4] H. Bradley, "Met. and Chem. Eng.," 1915, p. 841.

potash from plant ashes and gives analyses of the ash of various trees. He suggests that the waste from the sawmills in the Western States of America should be used for this purpose. Although a large quantity of this is sold for fuel purposes, there is still a considerable amount which cannot be utilized, sufficient to produce 1000 tons of potassium carbonate per annum. After leaching the ash with water the solution could be evaporated economically in an Enderlin type of evaporator fitted with a rotary roaster, similar to those used in the recovery of soda from the waste lyes of cellulose factories.

H. F. Zoller,[1] also writing on this subject, states that from 1 lb. of the ash of Douglas fir mill waste taken from an incinerator extracted 24 hours with water at 80° to 90° C., 3·2 to 4·8 grms. of potash (K_2O) were obtained, and from cedar wood ash 1·4 grms. The ash contained much unburnt charcoal and sodium chloride, sometimes to the extent of 16 per cent.

Such waste as banana stalks and skins might be burnt for the production of potash. R. H. Ellis[2] gives the following analyses to illustrate the value of these wastes:—

	Banana Stalks.	*Banana Skins.*
Dry matter	7·3 to 8·4	11·8
Water	92·7 to 91·6	88·2
Ash	1·5 to 2·4	1·77
Potash (K_2O) in ash	0·9 to 1·14	1·05
Ash in dry matter	20·5 to 29·9	15·00
Potash ,,	12·35 to 13·73	9·03
,, in ash	59·1 to 45·9	57·16

The ash of the stalks also contained 31·11 per cent of carbonic acid and only a trace of soda.

Potash from Molasses.—Molasses contain a considerable proportion of salts, notably potash salts, and more particularly is this the case with beet root molasses. Although a considerable quantity of potash has in the past been produced from this source,[3] it is, however, a very wasteful process to burn the molasses to an ash, since the large proportion of sugar which they contain is wasted. The potash salts could, however, be recovered from the spent wash of distilleries where molasses are employed, and as this is not utilized at all at the present time there is plenty of scope for some economical method of treatment with this object in view. There is, however, another method of treatment, devised by Wilkening,[4]

[1] H. F. Zoller, "Jour. Ind. Eng. Chem.," 1916, p. 105.
[2] R. H. Ellis, "Jour. Soc. Chem. Indt.," 1916, pp. 456, 521.
[3] 24,000,000 kilos of salts from this source were refined in France in 1890, ("Jour. Soc. Chem. Indt.," 1891, p. 282).
[4] J. E. Brauer, "Central. Kunstdüngerind," 1915, p. 242.

in which the molasses are treated with peat dust and the mixture innoculated with azotobacter, whereby the betaine is destroyed and the objectionable stickiness thus removed. The fermented material contains about 25 per cent of water, 3·75 per cent of nitrogen, 9·75 per cent of potash, and 45 per cent of humus. The amount of phosphoric acid can be raised by adding superphosphate, and such a fertilizer might be made having the composition: water 25 per cent, nitrogen 3 per cent, potash 75 per cent, phosphoric acid 3 per cent, and gypsum 9 per cent.

Practical tests have been made with such a fertilizer and the results are reported as quite good. The author states that it would be possible to produce about 350,000 tons per annum of this fertilizer in Germany.

Potash from Seaweeds.—Seaweed has been used in its green state as a manure both in Scotland and Ireland for a long period. Prior to the development of the alkali industry the ash of seaweed (kelp) also formed one of the chief sources of alkali used in soap and glass manufacture; this industry has, however, been discontinued, although a certain amount of kelp is made for the extraction of iodine. Both potassium salts and iodine are absorbed by seaweeds and are held with the greatest tenacity, thus it is stated by Merz that the algae *Nereocystis* and *Macrocystis* absorb far more potash than soda from sea-water and that the efflorescence which appears on the dry fronds consists of almost pure potassium chloride. The ash of the "sea lettuce" contains 45 per cent of potassium chloride,[1] and it has been proposed to propagate these species where the conditions are favourable to their growth.

Owing to the large amount of water which seaweed contains, it would not pay to transport it in that state to any considerable distance, for this reason it would be necessary to extract the most valuable constitutents at some factory as near the gathering grounds as possible. Seaweed contains about 80·44 per cent of water, 9·25 per cent of organic matter, and 10·31 per cent of ash. The organic matter contains 0·45 per cent of nitrogen, and in the ash there is 2·3 per cent of potash (K_2O) and 0·47 per cent of phosphoric acid.[2] The giant kelps of the United States lose 85 per cent of their weight when air dried, and contain in that condition 10 to 15 per cent of potash as KCl, 1 per cent of nitrogen, and 0·5 per cent of phosphoric acid.

As pointed out by J. Hendrick,[3] the seaweeds growing around the coast of the United Kingdom may be divided into two categories, those growing between low and high water mark, known as black

[1] C. G. Cresswell, "Jour. Soc. Chem. Indt.," 1915, p. 388.
[2] S. Macadam, "Jour. Soc. Chem. Indt.," 1888, p. 79.
[3] J. Hendrick, "Jour. Board of Agric.," 1916, p. 1095.

wrack, bladder wrack, and cut weed, belonging to the order *Fucaceæ*, and those growing in shallow water below low water mark, known as drift weed or tangles, belonging to the order *Laminariaceæ*, the most important of the latter being *L. digitata*.

The average composition of the dried seaweeds is given in the following table:—

	L. digitata.		*L. stenophylla.*		*F. vesiculosus.*	*F. nodosus.*	*F. serratus.*
	Stems.	Fronds.	Stems.	Fronds.			
Organic matter	64·03	77·28	64·73	77·76	79·71	78·39	77·56
Soluble ash	27·98	17·30	29·00	18·84	16·08	16·90	17·30
Insoluble ash	7·37	4·59	5·73	4·13	3·30	4·14	4·53
Silica	0·66	0·82	0·53	0·26	0·92	0·57	0·62
Nitrogen	1·31	1·30	1·02	1·08	1·18	1·13	1·50
In soluble ash:							
Potash (K_2O)	10·49	5·25	12·35	4·49	3·07	2·52	4·18
Soda (Na_2O)	5·35	4·24	4·91	4·91	4·51	5·78	4·85
Sulphuric acid (SO_3)	2·94	2·97	1·77	2·42	5·71	5·46	3·95
Total halogen as Cl.	9·92	6·11	11·28	6·56	3·44	3·50	4·70
Iodine	0·54	0·38	0·32	0·29	0·04	0·09	0·05

It will be seen from the above analyses that if drift weed were simply dried and ground it would form a fairly efficient manure, since, in addition to the organic matter, it contains about 10 per cent of potash and over 1 per cent of nitrogen. *L. digitata* is also valuable as a source of iodine, one ton of ash from the stems yielding 33 lb. and the same amount from the fronds yielding 40 lb. of that element. The fuci are less valuable, but at the present time it would pay to burn them for ash.

	Area. Sq. mile.	Fresh Cut Kelp. Annually. Tons.	Potassium Chloride. Tons.
Cendros Island to San Diego	91·4	16,979,800	649,000
San Diego to Point Conception	97·9	18,195,300	696,000
Point Conception to Cape Flattery	36·2	4,377,400	167,000
Puget Sound	5·0	520,000	20,000
South-East Alaska	141·6	15,666,000	598,000
Western Alaska	17·9	3,367,000	136,000
Total	390·0	59,105,500	2,266,000

The possibility of the utilization of seaweeds has been very exhaustively examined in the United States, where enormous quantities of seaweeds are to be obtained. In a United States Government Report[1] particulars are given, reproduced on opposite page, of the extent of the beds on the Pacific Coast:—

The average figures for the various kelps are as follows:—

	Macrocystis pyrifera.	*Nereocystis luetkeana.*	*Alaria fistulosa.*
Potash (K_2O)	12·59	20·1	9·1
Nitrogen	1·57	1·9	2·6
Iodine	0·23	0·13	trace

The amount of potassium chloride which could annually be extracted from this harvest of seaweed is thus five times as much as the total imports of potash salts from Germany.

It is calculated that at San Diego and neighbourhood, for instance, the cost of handling, drying, grinding, storing, and loading would not exceed $1 per ton of dried kelp, cutting and collecting $1·83, and general expenses $1, total $3·83. On the other hand, the value of the kelp would be $15·75 per ton, of which $9 would represent the potash value. If these figures are correct the margin of profit is sufficiently great to stimulate this industry and thus build up a national potash fertilizer industry. It was reported in 1916[2] that a plant on a commercial scale was about to be erected by the U.S. Department of Agriculture for the treatment of kelp and extraction of potash, including the most modern forms of drying kilns, distillation plant, etc., capable of dealing with 200 tons of wet kelp per day.

It has also been proposed to propagate such varieties of seaweed as *Pelagophycus porra* (egg), which are known to be rich in potash. The latter species being found in certain areas along the coast of Lower California..

There are on the Pacific Coast several factories turning out dry seaweed for agricultural purposes to take the place of low grade potash salts, and, according to another official estimate, 6,000,000 tons of potassium chloride per annum could be obtained from them on that coast. Potash obtained from the kelp of the Pacific Coast was marketed in 1915.

Kelp is prepared at several places on the Irish Coast, the exports amounting in 1912 to 4719 tons, valued at £18,300, and in

[1] F. K. Cameron, "U.S. Commerce Report," No. 143, June 19, 1915.
[2] "Board of Trade Journ.," Dec. 14, 1916.

1913 to 3939 tons, valued at £16,631. In Norway and also in Japan potash salts are likewise prepared from seaweeds, the annual production in Norway being about 1000 tons, containing 34 to 37 per cent of potash (K_2O).[1] Japan, which until recently was an importer of both potash salts and iodine, has now become an exporter.

According to J. H. Norton[2] the possibility of utilizing the vast deposits of seaweed in the Sargasso Sea of the Central Atlantic has been considered. This material is drifted into the West Indies, and cast upon the shores of the Bahamas in enormous quantities. In at least one harbour the accumulation becomes so dense at times as to considerably hamper and even almost to stop all navigation. It has been found that this seaweed contains on an average 9 per cent of potash as compared with 18·9 per cent in the kelp from the coast of California.

With regard to the collection and treatment of seaweed an interesting account was given by J. F. Lauches[3] of the methods adopted at Puget Sound. The kelp (*Nereocystis luetkeana*) is cut by a series of knives which are operated from a "scow" towed by a tug. At high tide one of these appliances will cut 100 tons of green kelp in 6 hours, and at low tide its capacity is increased.

By harvesting the seaweed direct from the sea contamination with sand is avoided; the latter causing the loss of potash and iodine when the kelp is burned. Also it ensures a continuous harvest, whereas the old system of collecting from the shore was only remunerative after large quantities of the weed had been cast up by rough seas and high winds.

From the "scow" the cut material is removed by a conveyer to a chopping machine which comminutes it, and thence by another conveyer to the deck of the tug. Unloading is performed by hand labour delivering the material by means of a conveyer to storage bins on shore. The seaweed contains in its wet condition about 92 or 93 per cent of water, and owing to the pressure of the material in the bins much liquid containing potash salts is squeezed out. The residue is finely shredded and then deprived of most of its moisture in a direct heat rotary drier, provided with dust chambers. The material as it emerges is sufficiently fine to be mixed directly with other fertilizers. In order to prevent any loss of nitrogen the wet weed is fed in at the fire end and is passed at such a speed as to ensure its containing 5 to 10 per cent of moisture. The potash can be readily extracted by leaching with water, and with 80 per cent muriate at $35 per ton it is believed that the industry will be

[1] "Bulletin Imp. Inst.," 1915.
[2] J. H. Norton, "U.S. Cons. Rep.," No. 276, Nov. 24, 1915.
[3] J. F. Lauches, "Met. and Chem. Eng.," 1916, p. 304.

quite profitable. The costs are, for harvesting and unloading the green kelp, 49 cents, and drying, 25 to 50 cents.

The old method of treating the weed was to expose it to the air until it was sufficiently dried and then burn it in heaps. The ash was then leached for the extraction of the soluble salts. Delaval[1] in 1767 obtained a patent for burning the wet weed in reverberatory furnaces with wood or coal. E. C. C. Stanford[2] proposed to dry the weed, press it into cakes and then distil it in retorts. The charcoal was cooled in closed receptacles and then leached with water to extract the potash salts and iodine. In addition tar water and ammonia were obtained in the distillate. Instead of burning the weed, Gignon and Gagnage[3] crush and press the weeds *Fucus giganteus* and *Zostera maritima* while in a wet state for the extraction of nitrogenous matter and salts. The residue is then boiled with a solution of soda ash, and the liquid is used in a subsequent operation. It was proposed to employ the residual cellular tissue for paper-making.

Stanford[4] also proposed to treat the weed with hot or cold water and evaporate the solution to dryness. The residue was then carbonized and extracted with water for the recovery of potash and iodine. The pulp was subsequently boiled with alkali for the production of a gummy material, which was known as algin. Boberg and Testrup[5] have been granted a patent for the treatment of seaweeds, which consists in mincing and pulping the material, heating in a closed vessel at 170° C. for twenty minutes and then pressing. This results in the formation of a good solid press cake and a liquor containing 70 per cent of the original alkali salts, 90 per cent of the iodine, 33 per cent of the nitrogen, and 10 per cent of the organic matter.

C. A. Higgins[6] is not very hopeful as to the future of the seaweed industry, since the methods of collecting and incineration are comparatively costly and will only continue while the cost of potash salts rules high. He refers to a method of treatment which has been successfully operated by the Hercules Powder Co. at San Diego, California, since 1915. In this process the material is fermented and the liquid neutralized with limestone. Three stages of the process may be discriminated. In the first, calcium acetate and potassium chloride are the chief products, in the second calcium salts of acetic, propionic, butyric, and valeric acids are obtained, while in the third most of the potassium iodide is extracted. The further treatment consists in heating the mixture of calcium acetate and potassium chloride whereby acetone and

[1] Eng. Pat. 870, 1767. [2] *Ibid.*, 1411, 1861. [3] *Ibid.*, 2741, 1865.
[4] *Ibid.*, 142, 1881. [5] *Ibid.*, 1766, 1914.
[6] C. A. Higgins, "Chem. and Met. Eng.," 1918, p. 432.

acetone oils are distilled off and the residue is leached with water to extract the potassium chloride. The mixture of organic salts is distilled with alcohol and sulphuric acid for the production of esters, and the iodine is obtained from the third product by treatment with chlorine and sublimation. The author states that probably the total production of potash from seaweed in the United States at the present time does not exceed 25 tons of 80 per cent potassium chloride per day, and that more than half this is obtained as high grade salt (95 per cent KCl) by the fermentation industry.

Potash from Wool-Scouring Waters.—Raw wool contains, along with the natural fat or "yolk" and dirt, a very appreciable amount of potash salts. When the wool is cleansed by washing with soap and water the potash salts pass into solution and help to form an emulsion with the fat, the liquid in many cases being run into the nearest stream or drain as the quickest method of getting rid of it. This wasteful process, however, has not been altogether universal and many methods have been tried for the extraction of the valuable products which it contains. The best and most rational method of treatment is to extract the wool with volatile solvents, the chief difficulty in this case being the great bulk of the material to be treated, the consequent size of the apparatus required, and the very large amount of solvent to be employed; but when such plan is adopted the grease is very quickly removed and the potash salts are left practically untouched, to be subsequently extracted by water, and, after roasting, they form a fairly pure kind of potassium carbonate without further treatment. In the Bradford district the raw wool, containing 40 to 50 per cent of grease and dirt, and approximately 4 per cent of potash, is washed in warm soap and water in two series of bowls, each series comprising four bowls. The soapy liquid is run into large brick-lined tanks excavated in the ground. When a tank is sufficiently full, sulphuric or hydrochloric acid is added in the proper quantity to decompose all the soap, whereupon a separation of fatty acids and wool fat takes place. The water is then drained through a layer of fine cinders, and after a time a considerable layer of grease accumulates on the latter and is removed with the spade. The grease is placed in filter bags, which are heated and pressed, the clarified grease passing through the bags. This is known as wool greace or Yorkshire grease, and has a ready sale. The liquid from these tanks is usually run into the nearest stream. In the Smith-Leach process,[1] however, the wool-grease, which is merely in suspension, is removed by centrifugal means and the liquid is evaporated and used again for scouring. In this way it becomes more and more rich in potash salts and can

[1] "Jour. Soc. Chem. Indt.," 1903, p. 851.

be treated for their recovery. This process was in operation at Bradford until a few years ago, but owing to changed conditions is not now profitable. According to Professor Gardner raw wool contains about 18 to 20 per cent of grease and 5 to 6 per cent of potash, but with the blend of wool now used it is only possible under the best conditions to get a liquid containing 4 per cent of potassium salts, whereas with the wool used in France, which is much more greasy, a 13 per cent solution can be obtained which will pay for the recovery of these salts. Large quantities of potash salts are in this way obtained in France, but the production is decreasing. In 1890 the total amounted to 4,000,000 kilos.

A review of the methods of recovering potash salts from wool-washing works has recently been published by R. S. Weston.[1] He states that previous to the war the only method of treating wool-scouring liquids of practical importance was that with acid, as above described. The potash in the liquids is then in the form of sulphate and is so contaminated with other salts that no process has yet been invented to recover it economically. In the precipitation process the waste liquors are allowed to stand for the settlement of sand and other solid impurities. The liquid is then passed through a centrifugal machine, which separates the fat and also the finer suspended matter. The clarified effluent is treated with chemicals which precipitates some of the impurities and the remainder of the grease, and the sludge thus formed is filter-pressed and dried. By extracting the dry sludge with solvents a low-grade grease is obtained and the residue is ground and added to fertilizers. The liquid from the filter is now sufficiently purified to enable the potash to be recovered from it, which is done by evaporation to dryness, calcining the residue in a rotary furnace and lixiviating the ash with water.

In a modification of this method, known as the Cardem process, the liquor from the centrifugal machine is sprayed through special nozzles into a series of chambers through which hot flue gases are passed. The process is divided into two stages, known as the "wet chamber," and the "dry chamber" respectively. In the wet chamber stage the liquid is simply concentrated, but in the dry chamber the concentrated liquid from the first is further evaporated until a perfectly dry product is obtained. For this purpose the liquid must be degreased by solvents, otherwise the evaporation is impeded. The dried product is very hygroscopic, but can be used as it is or after calcination; the potash salts may be recovered by lixiviation. The settled and degreased liquors may also be evaporated in specially designed evaporators, until it contains 65 per cent of solids, and then coked in an open furnace and the

[1] R. S. Weston, "Jour. Soc. Chem. Indt.," 1918, 17 T.

residue leached out with water for recovery of the potash. In some countries, as for instance in France, the so-called "de-suinting" process is followed; this consists in first soaking the wool in cold water, which dissolves the potash salts, which are then obtained by evaporation and calcination, the wool grease being subsequently removed with warm water and soap.

With regard to the cost of wool-scouring, the author states that the average wool-scouring plant usually has two trains of bowls which will discharge 12,000 gals. (U.S. measure) or about 200,000 lb. of waste per day. A plant for the treatment of this waste would cost at the present time, even with the ruling high prices, not more than $40,000. The 200,000 lb. of waste liquids would contain about 4000 lb. of grease and 2500 lb. of potash, and by treatment there would be recovered 2000 lb. of centrifugal grease, 1750 lb. of extracted grease, and 1600 lb. of potash. The balance sheet would then be something like the following:—

	Per diem.		Per diem.
Cost of centrifugal process . .	$45	2000 lb. of centrifugal grease at 10c. . .	$200
,, ,, evaporation . . .	48	1750 lb. of extracted grease at 8c. . . .	140
,, ,, degreasing . . .	35	1600 lb. of potash at 17·5c. . . .	280
,, ,, coking	17		
Management	20		
Total	165	Total . . .	$620
Daily profit .	$455		

The profit appears to be very large, but it is stated that one mill operating three trains of bowls is actually making a profit of $500 a day on centrifugal grease alone.

CHAPTER XVII.

TRANSFERENCE AND HANDLING OF RAW MATERIALS AND FINISHED PRODUCTS.

THE economic handling of raw materials, fuel, and finished products is one of the most important problems which the manufacturer—desirous of coping with the increasing competition—has to solve. But until recently it was exceedingly difficult to find a universal system of automatic transport adapting itself to the varying exigencies of different factories, and for a long time it was only possible to devise special installations for each case according to the nature of the materials to be conveyed. To difficulties of this nature was further added another arising from the plan of the factories themselves. The greater part of them, as is well known, had a very modest beginning. They have developed gradually, and have increased their production in a measure quite out of proportion with the working space at their disposal, so much so that there is no room for installing conveyers. These are reduced to the installing of lifts and small rails of the Decauville type. The systems used for conveying raw materials already warehoused or to be warehoused may be reduced to three: the continuous system, the funicular suspended rails, and the electric suspended rails, which hardly go back twenty-five years. The continuous system is already known, having been in use for a long time in all industries. It will suffice to point out a very neat improvement which has lately been made by Ad. Bleichert and Co. In continuous systems, whether the conveyers are bands or cups, work is confined to the same plane. All cup or chain conveyers known up to now, other than those on the Ad. Bleichert and Co's system, have the draw-back of working in the same plane, and consequently entail a transhipment of the materials when it is desired to convey the materials in different planes. This transhipment entails costly plant, consumes motive power uselessly, and exhausts the material. The mono-rail cup system of Ad. Bleichert and Co. suppresses these drawbacks, for the cup-chain continues to pass from one plane to another by the aid of suitable guides. Fig. 54 shows a section of the cups of this ingenious system. Figs. 55 and 56 are photographs of installations of this system at work. Fig. 57 is an application of this cup-chain to the handling of fuel

and raw material in a chemical factory. This firm has likewise brought the electric automatic systems with intermittent charges to such perfection that they have spread enormously for some time back in Europe in metallurgical works and chemical factories. This process of automatic electric handling consists in causing an automatic car (to which is suspended a bin) to convey the material to run over an aerial railway. The current is led to this electric car by a bronze wire. Fig. 58 represents this system, which has this great advantage, that any desired shape may be given in a horizontal plane to the rigid aerial railway, so that it can go round the multiple obstructions which it meets not only in old factories but even in those still under construction. An electric automotor truck, such as is shown in Fig. 58, can turn in curves of two metres radius. The Americans, it is true, were the promoters of a system called "Telpherage," which was likewise

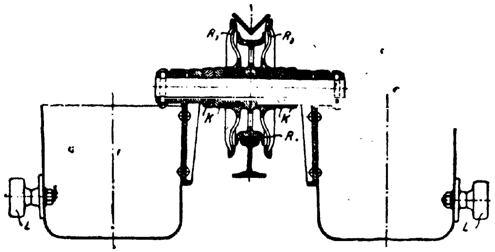


FIG. 54.—Section of Elevating Cups (Ad. Bleichert and Co.).

based on the conveyance of heavy unitary loads on rigid, robust aerial railways suitably supported, but the principal obstacle to the extension of their system was that it barely attained a yield of 12 per cent, due to the want of proportion existing between the weight of the rolling car and that of the useful load to be conveyed. These weights were in fact in the ratio of 5 to 1. But if the first thing to be done was to reduce the weight of the car and the bin which form the truck as much as possible, taking into account the safety of the workmen, it was necessary also to create from the triple point of view of economy, simplicity and rapidity of transport all the other parts of a complete installation. The plant and rolling stock for transport, such as the exigencies of modern factories demand, should include points and automatic safety apparatus, and above all the automatic travelling of the individual wagons independent of any handling, as well as the greatest possible speed. The system devised by Ad. Bleichert and Co., owing to the ingenious arrangements of its rails, points, and curves, combines this associa-

FIGS. 55 and 56.—Electrical Conveyers (Ad. Bleichert and Co.).

tion of the greatest possible speed with the automatic working of the trucks, and certainly the solution of the problem should attract the attention of manufacturers, for it effects a remarkable saving in the working expenses of factories, particularly in chemical works. When the railway is on a level, a single motor suffices, the rigid rail being generally fixed on a level. But in most cases it is necessary to span a difference of level between the point of departure and the point of arrival. It would be, moreover, very onerous to wish to employ a uniform slope throughout all the path of the railway, for it would involve a considerable expenditure of energy and a costly constuction.

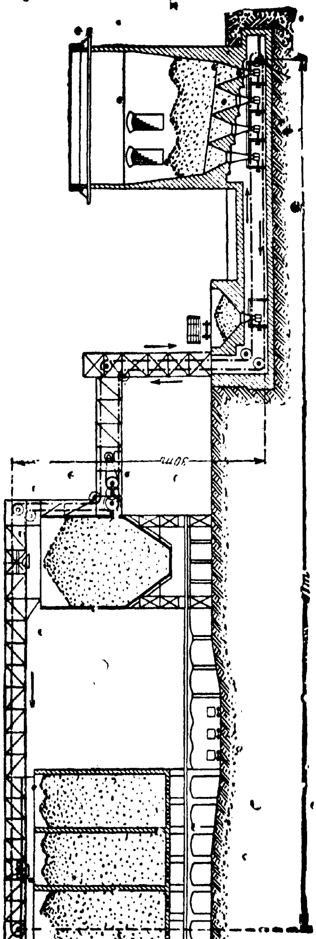


Fig. 57.—Cup-chain Elevator at work transhipping Coal in a Chemical Factory (Ad. Bleichert and Co.).

The Bleichert system overcomes the difficulty in a practical manner by interposing in the network, suspended on bearings, trunk ways with desired incline, spanning the out of level, whilst preserving enough free space to allow the wheels not to lose contact with the railway, and the bins to maintain their natural movement of oscillation. The advantage of this system consists especially in the fact that the limit need not be taken into account, for the sections are spanned by aid of organs absolutely independent of the driving of the cars. For this purpose the carrying track becomes a strong stair and rejoins in a

few metres an upper part on bearings, and on this stair the car is not driven by its own motor. A special system consisting of a motor and a chain or cable, running above the rail on the stair, pulls the car along in the following manner: A hook fixed in the car catches the chain which drives the fixed motor of the stair. The carrying system is drawn up to the moment when the hook quits it, which happens when the car reaches the elevated part or bearings. When the car catches on the stair the current from its own motor ceases, whilst it puts the cable in motion by means of another special motor which animates it with a uniform

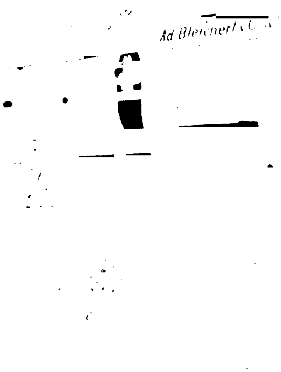


FIG. 58.—Electric Automotor Truck.

motion. At the moment when the car reaches the upper extremity of the inclined section, the inverse occurs. This manner of traversing the stair is very advantageous, as it permits a low-power motor to be used on the car. If the car motor had to ascend a considerable incline of itself, it would require to have a much greater force, hence a considerable weight increase of the section of the carrier, and consequently an increase of expense in the initial installation and working expenses (it would require in fact motors six to ten times more powerful per car). There are cases, however, where, in consequence of considerations special to the problem to be solved, it is preferred, instead of this mixed solution,

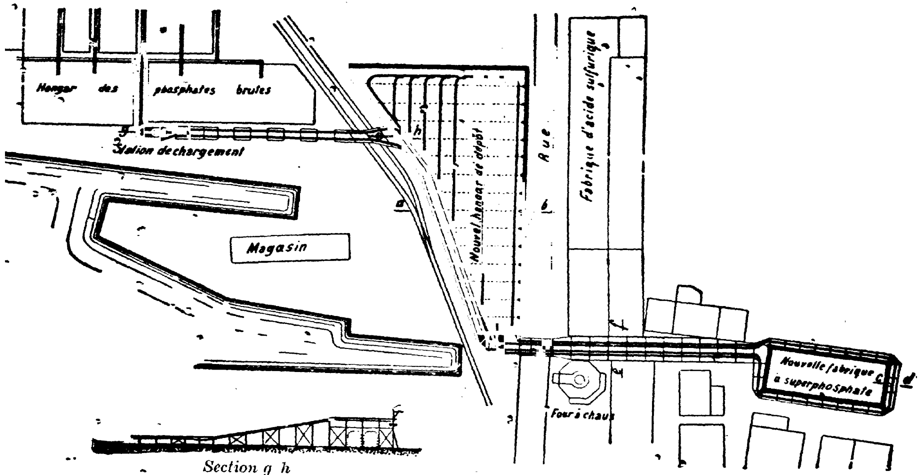


FIG. 59.—Electric Transhipment of Phosphate and Superphosphate in a Manure Factory.

Hangar des phosphates brutes = Raw phosphate shed. *Station de chargement* = Loading point. *Magasin* = rehouse. *Nouvel hangar de depôt* = New store shed. *Rue* = Street. *Fabrique d'acide sulfurique* = Sulphuric chambers. *Bâtiment du four à grevier* = (?) Pyrites kilns (burners). *Nouvelle fabrique à superphosphate* = New rphosphate factory. *Four à chaux* = Lime kiln.

to solve the problem of removing material by means of independent arrangements enabling each to surmount the difficulties encountered. Automatic handling installations can in fact be seen, consisting of a network of the system of cup-chain elevators combined with an electric network, or consisting of some one of these with the third system, that is to say, the funicular rope system. For example, Fig. 59 shows a conveying installation in a superphosphate factory in which very considerable differences in level had to be spanned. It was a question especially of conveying the raw phosphate discharged from ships into a shed through the whole factory by an overhead railway to bring it into the superphosphate factory situated behind, and to lift the superphosphate there and deposit it in a shed from which it is charged into railway wagons. In these transfers all handling had to be avoided. The superphosphate shed is connected with the factory by a cable conveyer starting from the

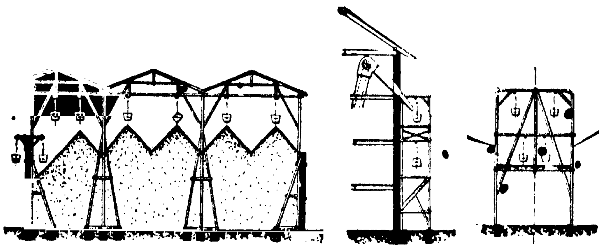


FIG. 60.—Section *a b* of Fig. 59. Section *c d* of Fig. 59. Section *e f* of Fig. 59.

point *g*, and reaching about 8 metres (26 feet) in height, going round the factory and bringing its bins into a discharging hopper, in which they are tip-tilted. The finished superphosphate is in its turn poured by means of an elevator into a hopper installed on the roof, from whence it is conveyed by means of an electric automatic superphosphate conveyer installed above the raw phosphate conveyer. The tilting of the bins in the hall of the depot, their return and their stoppage at the point of loading, are carried out in an absolutely automatic manner. Fig. 64 shows the system of rolling and of tilting the electric superphosphate bins above their depot; the sections of the figure (Fig. 60), *a b*, *c d*, *e f*, show the arrangement of the railways. There will be seen on the section *c d* the elevator described above, which serves to pour the superphosphate into the bins of the electric automatic system. This question of the elevation of material leads to the description of another method generally used to elevate material to levels capable of sometimes

reaching 10 metres (33 feet) of vertical difference in level. The system of rope traction of cars, ordinary or electrical, on a stair to be spanned such as that shown in the section g h of Fig. 59, can only be judiciously employed when the tonnage and the difference in level warrant it. For average tonnage and less, and for vertical differences in level up to about 6 to 7 metres, a special system of automotor car with crane is used, such as shown in Fig. 61. It will be seen in that figure that between the bin and the car properly so called there is geared an electric crane with its commutators, magnetic brake and different arrangements to render the whole of the necessary manœuvres automatic once the current is applied to the whole of the car. By this system and by the aid of complementary arrangements of the line, the whole of the car can be arrested in any desired point of its course to pass the current automatically from the upper translating motor to the lower motor of descent, and of lifting, driving the crane at will; automatically to tilt the bin of its contents by the action of the electro-magnet and its lifting crane, after which the empty bin, coming to its highest position, acts at the same time on a contact which again causes the current to pass from the elevating and descending crane to the propelling crane, and the whole of the car starts in motion again, to return to the place where the bins are filled. The latter are filled by themselves at the hopper by a manœuvre, say, exchanged against others filled between times in the course of the journey of the preceding ones. In general, these automotor cars consist of two cheeks of cast-steel firmly held together by cast-iron cross-pieces, between which are lodged crucible cast-steel pulleys with deep grooves, the bosses of which turn freely on axes of phosphor bronze acting as lubricating reservoirs. A wheel gearing with the steel pinion of the electric motor is fitted on the outside of one of these pulleys, and on the boss of the other a brake pulley is mounted, the band of which, stretched on a powerful spring, on the type of a coach-spring, is automatically liberated when at work by an electro-magnet. There are a very large number of these types of electrical cars, so as to respond to the different problems occurring in industry. For example, Fig. 62 shows a

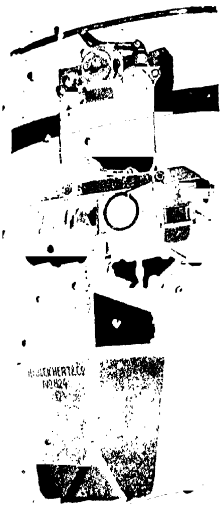


FIG. 61.—Special Automotor Electric Car with Crane.

special system of car for spanning very sharp curves. There will also be seen from the figure the difficulties which had to be surmounted in a factory the free space of which at this point is restricted, as shown in the engraving. It also shows the use of bins with bi-

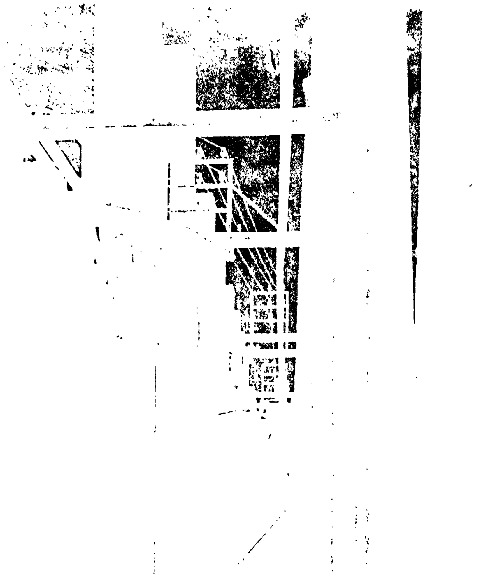


FIG. 62.—View of Special Electric Car Conveying System turning rapid curves.

lateral discharge by the unlatching of the system of closing of their side doors. Fig. 63 shows a bin of this system hooked to a special car with a specially arranged crane, which is used in the siloing of

various materials before being fed into the different hoppers. It will be seen that the bin shown in the engraving is fitted with a four-wheeled truck which enables it to run on Decauville rails in

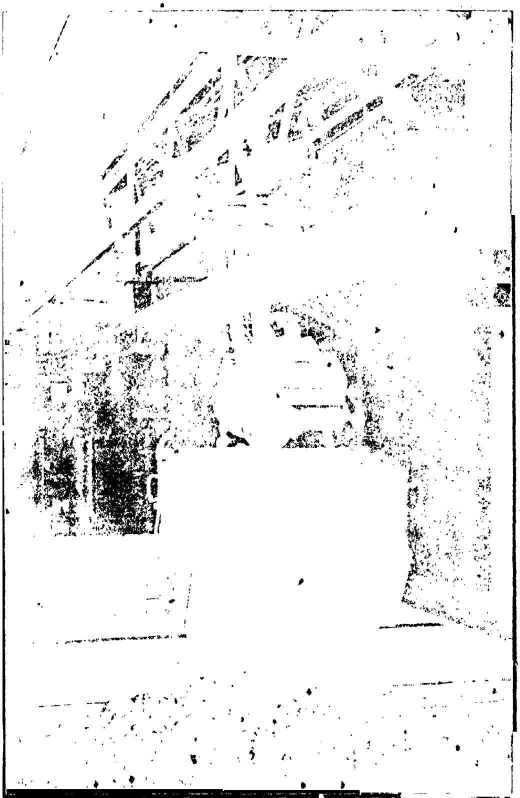


FIG. 63.—Electric Conveying Car at Silo.

the space through which it proceeds to the filling of the bins. The most important points of this system of electric traction must be described. If the railway is straight the speed may reach 2 metres (6 ft. 6 in.) a second. But this is not generally the case. A system often contains very sharp curves, in which the car and the suspended

bin ought to have a much lower speed than that given above. It will be seen that the centre of the system in motion, being much lower than the railway on which it rolls, centrifugal force corresponding to the speed of 2 metres per second would cause the system to deviate appreciably from the vertical, which might cause mishaps. To obviate this, in the Bleichert system resistances are fitted on the conductor at the passage of curves, so as to diminish the speed only in the curved part of the course; in the straight lines the speed is a maximum. Another peculiarity consists in the arrangement of the points; so long as the apex of the points is not well closed a commutator electrically isolates on the opening of the latter a certain length of conductor up to the points itself. The car then becomes stationary in front of the points if these are badly shifted, which avoids accidents. The length of this insulated trunk is such that the truck cannot reach the points in virtue of the acquired speed. When it is not a case of heavy freights, the most practical system is that in which the trucks accomplish a double journey on the same line; but in the case of important installations the railway is arranged in a circuit, so that the trucks can circulate in the same direction and follow each other continuously. So as to stop or start the trucks at any desired point, the naked conductor which transmits the energy to the trucks is divided into sections, insulated the one from the other, and, as need be, such and such sections are brought into circuit or out of circuit by simple commutators working automatically, which can be placed at any necessary spot.

The division of the line into separate sections has the advantage of forming a block system, which prevents any collision automatically, and any shock between the trucks at the points or the crossings. Each truck reaching a section interrupts automatically by means of a commutator the current from the section it has just quitted, so that the wagon following, arriving on this section, which is thus out of circuit, stops of its own accord. As soon as the first of the trucks just described arrives at the end of the section which we have seen it enter, it automatically turns a commutator, which re-establishes the current on the section on which the following wagon is standing, which can in this way continue its journey, repeating the preceding operations in the same cycle for the truck following. In that way no truck can reach crossings and points until the wagon which precedes is at a sufficient distance, and before it can pass them in its turn.

This arrangement, indispensable to any suspended electric railway on which a regular and safe service is required, produces at certain points—for example, where the trucks are filled—the following effects. The truck reaches the spot where it is filled, stops automatically, the current on the section on which it is placed having been cut by the truck ahead. The workman, the only one

generally required for operating these installations, opens the valve which shuts the hopper, thus allowing the matter to run into the bin, and after having received its charge, brings the section into circuit. If, owing to fortuitous circumstances, the loading of the truck takes rather long, a large number of wagons would arrive, but it would be impossible for them to advance owing to the blocking of the line, and they would be forced to arrange themselves at regular intervals along the line. As soon as the charged truck

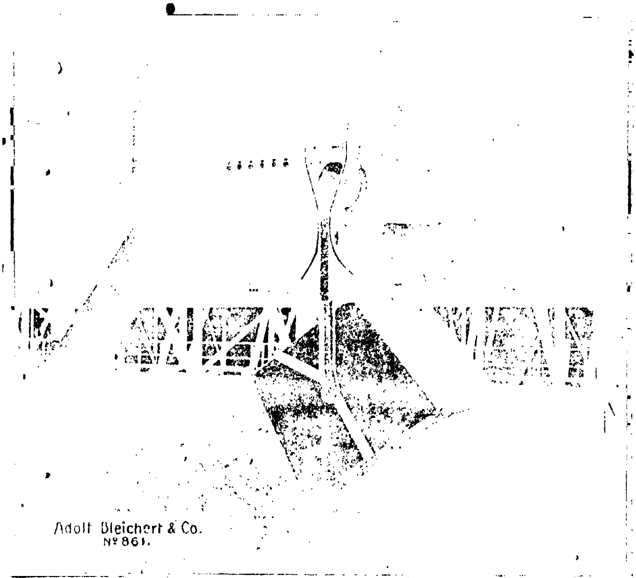


FIG. 64.—Electric Conveying Car tilting Contents into Silo.

starts, the following one advances automatically and stops at the hopper to receive its charge. The other trucks follow the lead and advance one after the other until their turn comes to take their place at the hopper, and the same routine goes on continuously.

As already mentioned, all supervision during the journey is absolutely superfluous, the trucks are unloaded automatically, for the bolts which hinder the bin from tilting, or which keep the sides of the bin closed, unlatch themselves during the working by means of a bolt. Owing to these arrangements it is possible to obtain

great train on the whole line. These aerial railways on the electric automatic system may be supported outside the building on wood or metal brackets, leaving below them the necessary freedom for working in the factory and assuming, consequently, shapes appropriate thereto. At other times, as a measure of simplification or economy, these rails are hooked on to wall brackets or even to existing beams. Fig. 64 shows the automatic filling of silos by an electric railway suspended from old wooden beams, whilst Fig. 63 shows that the automatic electrical railway has been suspended from new metallic structures. The system of bin and car of Fig. 64 is a stout thick-set system in a vertical direction, taking into account that the old wooden beams of factories are at this point surbased, that they only allow of a small heap, and that thus all economy in the vertical height of the plant installed is particularly appreciated. On the other hand, in a new building like that of Fig. 63, the necessary vertical height can be calculated at leisure, profiting in the designing of the plant by the

FIG. 65.—General Arrangement of Electrical Conveying Machinery in Pommersdorf Chemical Factory.

advantages of a sufficient height to instal an appropriate system of transport. This system, so remarkable and so simple in itself, insures the conveyance with a minimum of handling of big tonnages in as automatic a manner as possible.

The *Compagnie St. Gobain*, Chauny et Cirey, has just erected at its Chantenay chemical works near Nantes an important installation of this nature. The photographs (Figs. 65-66) show as a whole similar installations in chemical factories and superphosphate factories. The first is the Pommersdorf chemical factory and the

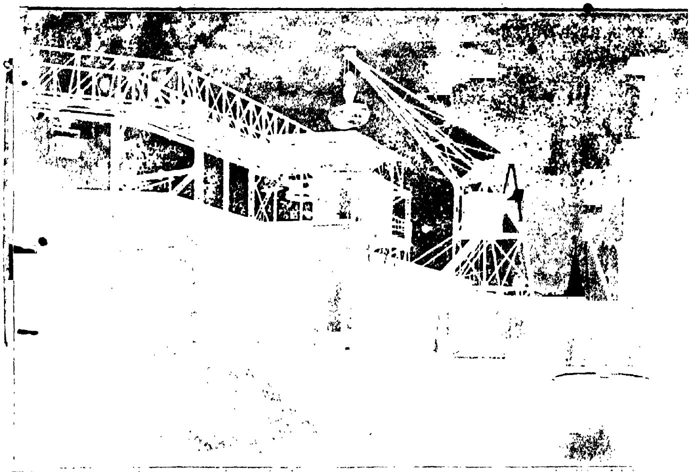


FIG. 66.—General Arrangement of Electrical Conveying Machinery in Emmerich Chemical Manure Factory.

second the Emmerich chemical manure factory. These automatic conveying installations in factories where quantities of material are treated are of capital importance for go-ahead manufacturers desirous of lowering their wages bill and to place themselves as far as possible beyond the risk of strikes. It would lead us too far to develop all the applications which can be made of this system, the more so as each new problem leads to a new solution. It is to be hoped that enough has been said for readers to have at their finger-ends all the advantages of these new systems, which not only are already spread throughout France, but have more especially a considerable development abroad. We cannot terminate this slight

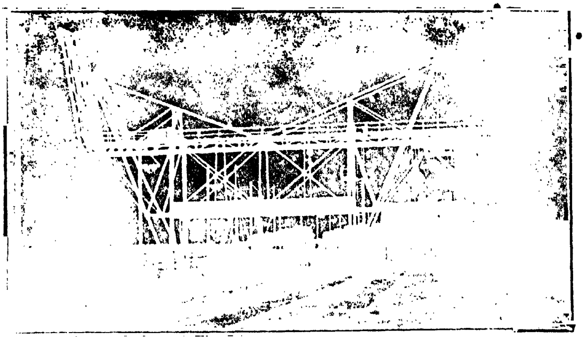


Fig. 67.—Electrical Transhipment Plant, St. Gobain's Chemical Factory, Boucau.

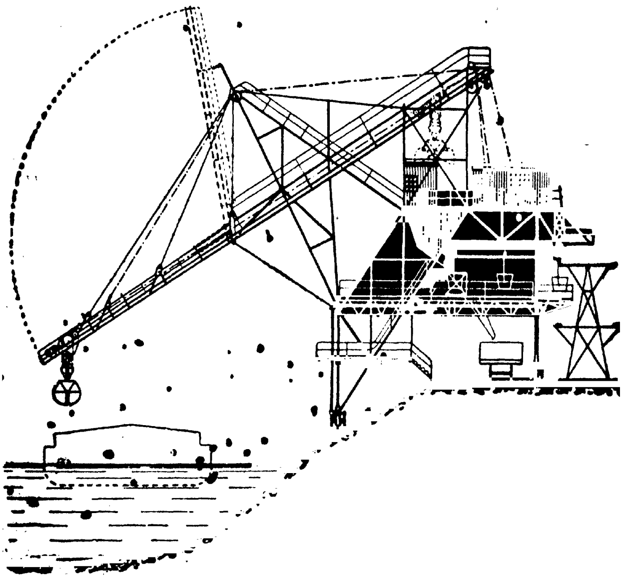


Fig. 68.—Electrical Transhipment Plant in a German Factory.

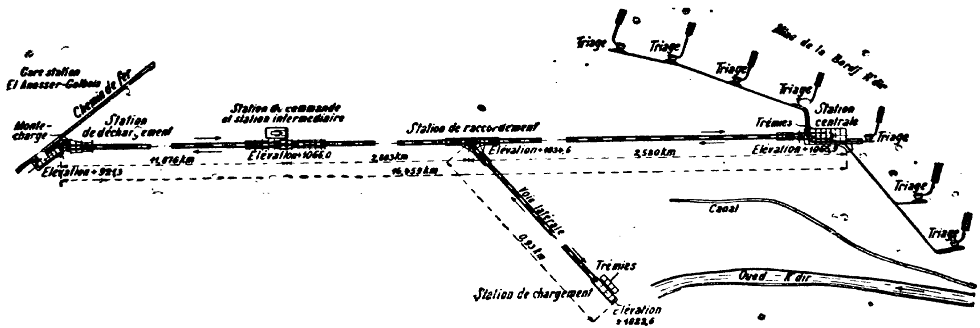


Fig. 69.—Cable Transhipment System of Algerian Phosphate Factory.

Gare station = Railway station.
Monte-charge = Elevator.
Station de commande et station intermediaire = Power station and intermediate station.
Station de raccordement = Marshalling station.
Mine de la Bordj R'dir = Bordj R'Dir phosphate mine.
Voie latérale = Branch line.
Oued R'dir = River of that name.
Chemin de fer = Railway.
Station de déchargement = Unloading station.
Trémies = Sieves.
Triage = Assortment.
Station de chargement = Loading point.

review of these automatic conveyers without bringing to mind that the question of the automatic conveyance of raw materials from the ships or wagons in which they arrive is likewise an important question, especially for large factories. Fig. 67 shows the view of an automatic conveyer installed by the *Compagnie St. Gobain* at its Boucau chemical factory. Fig. 68 shows a conveyer of this nature installed for a German factory of chemical products by Ad. Bleichert & Co. Sometimes, as will be seen in Fig. 67, the cargo discharged from ships is simply disgorged by tilting-bins or slings into fixed or rolling hoppers or into rolling stock, or sometimes, on the other hand, these automatic transhipping installations are continued by automatic conveyers like those described above. The attention of those working phosphate deposits is drawn to the rope system adopted by the *Cie Centrale des Phosphates à Paris* for working its deposits of Bordj R'Dir.

There will be seen in Fig. 69 a considerable development of these rope railways which collect the phosphate into the great warehousing hoppers at the railway station of El Anasser Galbois, Algeria. Local considerations, the price of labour, the greater or less tonnage to be discharged and handled, the regular or intermittent manner in which these transhipments or shiftings occur, can alone afford, in each case, the necessary data to solve the problem in the most satisfactory manner in the interests of the manufacturer. The best course for manufacturers who occupy themselves with these questions more and more is to submit the problem to the study of specialists trained by constant practice.